# CHAPTER 7: THE EVERGLADES MERCURY PROBLEM

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## SUMMARY


### THE PROBLEM

The Florida Department of Public Health has issued fish consumption advisories for the Everglades to protect the public from exposure to the high mercury concentrations in some Everglades fish species. This has impaired the use of the Everglades as a sport fishery. The high mercury concentrations in the Everglades food chain may also threaten endangered species like the wood stork, mink, and Florida panther. Mercury is a problem in many rivers, lakes, and wetlands throughout the U.S. and the world, but the Everglades is one of the most contaminated aquatic ecosystems in North America.

Moreover, concerns have been raised that in the process of eliminating the eutrophication threat to the Everglades, the mercury problem could be made substantially worse. If this so-called "inverse relationship" between eutrophication and mercury bioaccumulation in fish is occurring to the extent predicted (Sugar Cane Growers Cooperative, 1999), this tradeoff might not be acceptable.

Why does the Everglades have a mercury problem? The inorganic mercury in rainfall, runoff, and peat soil is being converted by naturally occurring bacteria into methylmercury, a very toxic form of organic mercury. This is occurring at a higher rate in the Everglades than most other places, but the reasons for this are not yet clear. Once produced, methylmercury is absorbed by one-celled plants and microscopic animals that are eaten by small fish, and on up the food chain, to top-predator fish and birds. Methylmercury in water or food is readily absorbed, but only slowly eliminated from the bodies of fish. This process results in the (bio)accumulation of methylmercury in fish tissues. Eventually, methylmercury can build up to concentrations in top-predator fish many millions of times the concentration in the surrounding water. Fish-eating animals, and their predators, then further bioaccumulate this methylmercury to potentially toxic levels.

### THE SOLUTION

The mission of the District's Mercury Studies Program is to provide the responsible federal and state agencies with reasonable assurance of the following:

- There will be no substantial increase in the quantities of total mercury or methylmercury in runoff as a result of the adoption of Best Management Practices (BMPs) by farmers in the Everglades Agricultural Area (EAA).
- The Stormwater Treatment Areas (STAs) will not cause nor contribute to a new mercury problem within their borders or downstream.
- The planned reconfiguration of South Florida hydrology to meet the future water supply needs of humans, the Everglades, estuaries, and bays will not cause nor contribute to a worsening of the Everglades or Florida Bay mercury problems.
- All requirements of federal and state statutes, regulations, standards, and permits governing mercury pollution will be met.

To conduct this mission requires an understanding of the pre- and post-restoration as listed below:

- Supplies of mercury from EAA runoff, peat soil, and air deposition;
- Processes that link those supplies to the concentrations of methylmercury in Everglades fish and fish-eating animals;
- Influences of water quantity and quality on those processes; and
- Toxic effects to humans and wildlife when making full use of the Everglades as a sport fishery and wildlife habitat.

The District and DEP continue to support the multi-agency South Florida Mercury Science Program (SFMSP) to obtain the information and tools needed to understand and solve the Everglades mercury problem.

## POST-STA MERCURY IMPACTS

One of the most important objectives of the SFMSP is to predict what will happen to methylmercury production and bioaccumulation in the northern Everglades when the supplies of total phosphorus and mercury are reduced by the STAs, and eutrophication is eliminated. To achieve this objective, the District and its partners in the SFMSP pursued three separate but interrelated approaches discussed below.

1. **Reference Site Approach:** Evaluate the pre-STA mercury risks at an unimpacted reference site to approximate post-STA conditions in the already impacted area. Compare these risks to those at the most contaminated site as a positive control. The reference site selected for this purpose was WCA-2A-U3, where water column total phosphorus concentration already averages less than 10 ppb, but where hydrology and water chemistry were otherwise very similar to those in the already impacted area. Validate exposure and toxicity estimates against field observations. Use the validated exposure and toxicity assumptions to predict post-STA mercury risks.
2. **Statistical Modeling Approach:** Measure mercury in water, sediment, plants, and wildlife along with related water and sediment chemistry data at various Everglades sites to identify important influential factors using various statistical models. Test the predictive validity of these statistical models against real conditions at other sites in the Everglades. Use the validated statistical models to predict post-STA mercury risks.
3. **Mechanistic Modeling Approach:** Quantify the key processes and influential factors that govern methylmercury production and bioaccumulation in controlled experiments in the laboratory and field. Develop a mathematical model that includes all of these processes and influential factors in a realistic way. Fill key data gaps with literature values until Everglades-specific results become available. Test the validity of this realistic mathematical model against real conditions in other portions of the Everglades. Use the validated mechanistic model to predict post-STA mercury risks.

The results of all three approaches were summarized in Chapter 7 of last year's Everglades Interim Report. The first approach was conducted in Appendices 7-2 and 7-3, while Appendix 7-4 presented the second and third approaches.

Based on the first approach, the District concluded that it is highly unlikely that there will be an unacceptable increase in post-STA methylmercury risks to fish-eating birds. When the exposure estimates prepared for the Sugar Cane Growers Cooperative (Exponent, 1998) were corrected with Everglades-specific data, the two risk assessments were in substantial agreement. This correction analysis was conducted in Appendix 7-3 of last year's Everglades Interim Report. The District's probabilistic ecological risk assessment, **Appendix 7-3b,** reinforces last year's results and conclusions.

The results of the second approach revealed that there are a number of factors that could be influencing methylmercury production and bioaccumulation along the nutrient gradient in WCA-2A and elsewhere in the Everglades. The strongest influences on methylmercury production in the sediment appear to be pore water sulfide and total mercury in peat soils, while the strongest influences on methylmercury bioaccumulation along the WCA-2A nutrient gradient appear to be dissolved organic carbon (DOC), hardness, and total phosphorus in the water column.

However, it was concluded in Chapter 7 of last year's Everglades Interim Report that neither the District's two-variable statistical model, based on water column DOC and calcium, nor the one-variable statistical model, based on water column total phosphorus developed for the Sugar Cane Growers Cooperative, were valid for predicting post-STA mercury risks. This is because neither could accurately predict methylmercury bioaccumulation in mosquitofish at other Everglades sites using the appropriate water quality data. The results of this year's multivariate analysis of the influences of water and sediment chemistry on methylmercury bioaccumulation support last year's results and conclusions.

The third approach was conducted using a mathematical model built by the U.S. Environmental Protection Agency's (USEPA's) Office of Research and Development. It included everything that was known up to 1998 about methylmercury production and bioacccumulation in the Everglades, including the influence of water column total phosphorus on plant production and decomposition, and the accumulation of undecomposed plant matter called peat. These are the key elements of biodilution. The results of the pre- and post-STA modeling analysis indicated that there could be about 50 percent, but not an ecologically significant increase in methylmercury bioaccumulation in the already impacted area.

Further, there was a benefit to the reduction in post-STA mercury loads to the northern Everglades. Thus, there is likely to be a substantial margin of safety in the results of the first approach, which is based on a 10-fold increase in methylmercury bioaccumulation between WCA-2A-F1 and WCA-2A-U3.

## KEY FINDINGS FOR 1998

In Chapter 7 of last year's Everglades Interim Report (Fink et al., 1999), the District identified a number of important findings from the SFMSP:

- Mercury in Everglades peat soil has increased between three and six times since the late 1800s, so today's Everglades is unnaturally contaminated with excess mercury.
- Farm and urban runoff may be having localized impacts immediately downstream of District structures, but the general pattern of peat soil contamination suggests a more diffuse source.
- With rare exceptions, the Everglades marsh and tributary waters today are in compliance with the total mercury Class III Water Quality Standard of 12 ng/L (parts per trillion), but fish consumption advisories remain in effect, so the standard cannot be adequate.
- The Everglades Nutrient Removal (ENR) Project (**Chapter 6**), removed 50 to 75 percent of the mercury entering through the inflow pump station each year during its nearly five years of operating life.
- More than 95 percent of the mercury supplied to the Everglades each year is from atmospheric deposition, but the contributions of air pollution from local sources and worldwide background to that supply have not yet been adequately resolved.
- Methylmercury is produced from inorganic mercury from the air, water, and soil by sulfate-reducing bacteria in the top layer of the peat, but some production may also be occurring in the thick mats of algae, referred to as periphyton at some locations.
- Excess sulfate is present in the northern and central Everglades, so something other than

sulfate is likely to be limiting the rate of methylmercury production there.

- The District's assessment of the methylmercury threat to the wood stork, great egret, and great blue heron indicates that exposure is insufficient to cause a significant level of toxicity in these populations when they feed at WCA-2A-U3, an unimpacted reference site. This may not be the case at the methylmercury "hot spot" in WCA-3A, however.

## KEY FINDINGS FOR 1999

This year there are several important new observations:

- Operating the STAs with higher flows and deeper water during high rainfall years is likely to maximize the removal efficiency of both total mercury and methylmercury. (For a discussion of the STA optimization program, refer to **Chapter 6**.)
- Screening of several Advanced Treatment Technologies (ATT) has so far not revealed significant methylmercury discharge or mercury accumulation in solid residues. (For a discussion of the ATT program, refer to **Chapter 8**).
- Methylmercury production in peat soil tends to decrease as the amount of sulfide in the soil pore water increases, but the methylmercury production tends to increase as the amount of total mercury in the soil increases.
- The excess sulfate in the northern and central Everglades can be traced to the EAA, but there are still some uncertainties regarding the relative contributions of natural and cultural sources and historical and present-day cultural practices.
- Mercury concentrations in small fish are most strongly associated with total mercury concentrations in peat soil, suggesting the importance of peat soil and its inhabitants in the Everglades food chain.
- Classical biodilution is not occurring along the WCA-2A nutrient gradient, due to light limitation effects in the nutrient-enriched areas.
- There is some evidence that the concentrations of mercury in fish and birds at some South Florida locations have declined over the last decade.
- The District has refined last year's assessment of the methylmercury threat to wading birds by incorporating new Everglades wading bird toxicity and exposure data and using more advanced techniques, but the findings and conclusions remain the same.
- Clear field evidence of methylmercury toxicity to populations of highly exposed Everglades wading birds breeding near the WCA-3A "hot spot" has not yet been obtained by researchers.
- Otter feeding exclusively in the vicinity of he unimpacted reference site in WCA-2A are not likely to be at a substantial risk of methylmercury toxicity, but otter feeding exclusively in the vicinity of the WCA-3A "hot spot" may be.

## CONCLUSIONS

Last year's and this year's key findings support the following answers to six key Everglades mercury management questions:

1. The Everglades mercury problem remains significant, but there is some evidence of a downturn in mercury levels in fish and birds over the last decade at some Everglades sites.
2. Despite a reported 65 percent reduction in mercury air pollution from local sources over the last decade, there is still much uncertainty regarding the sources of the mercury depositing on the Everglades from air. Air pollution source, movement, and chemistry studies should substantially reduce this uncertainty over the next two years.
3. The reduction in mercury risks is best achieved by reducing mercury air pollution from local sources. The routing, timing, quantity, and

quality of water flowing into the Everglades will be optimized for the protection of Everglades structure and function, including endangered species habitat, so it is unlikely that there will be much flexibility for manipulating water quantity and quality to minimize methylmercury production and bioaccumulation, even if some options are potentially effective.

4. The District's updated ecological risk assessment continues to support last year's conclusion that it is highly unlikely that the operation of the STAs will cause or contribute to an environmentally significant increase in use impairment or mercury risks to fish-eating wildlife.
5. New monitoring, research, and modeling tools have been developed to conduct the studies needed to understand and solve the Everglades mercury problem.
6. DEP endorsement of the Everglades Mercury Action Strategy (E-MAS) is being sought to ensure that the restoration objectives and timetables in the Everglades Forever Act are met.

## RECOMMENDATIONS

To ensure that the District and DEP understand and solve the problem of toxic pollutants other than phosphorus, the Everglades Forever Act sets aggressive deadlines for evaluation, research, and permit application for source control to meet a revised mercury standard by December 31, 2006. The Act also recognizes the need to monitor the Everglades mercury response to the phosphorus reduction program. To fulfill the Act's mandates according to the E-MAS strategy, the emphasis of the SFMSP should now shift from defining the Everglades mercury problem to developing the regulatory targets and tools for solving it. The research should now focus on:

- Followup studies to better quantify the key processes and influences that govern methylmercury production and bioaccumulation
- A model that relates the methylmercury concentrations in water, sediment, fish, and birds to the rate at which mercury is supplied to the Everglades from all sources
- A revised numerical standard for total mercury to protect fish-eating animals and their predators, including the endangered wood stork and Florida panther.

The required monitoring, research, and modeling projects are now planned or already under way.

# INTRODUCTION

The Everglades has a mercury problem (Ware, 1989). The use of the Everglades as a sport fishery has been impaired, because the Department of Health has issued a health advisory recommending limited fish consumption in Water Conservation Area 1 (WCA-1) and no fish consumption for the rest of the public Everglades and the Everglades National Park (Park). The limited fish consumption advisory also includes Big Cypress National Preserve and Eastern Florida Bay. The advisory map from the Florida Game and Wildlife Conservation Commission is reproduced in **Figure 7-1**. The excessive mercury concentrations in fish may also threaten some wildlife populations. The pattern of contamination suggests that fish-eating animals and their predators feeding in the middle of WCA-3A are likely to be the most highly exposed (**Figure 7-2**). However, the numerical Class III Water Quality Standard for total mercury of 12 ng/L is not being routinely exceeded at any of the sites monitored in the District's canals (**Appendix 7-2**). As reported in Chapter 7 of last year's Everglades Interim Report, DEP has concluded that the total mercury standard is deficient.

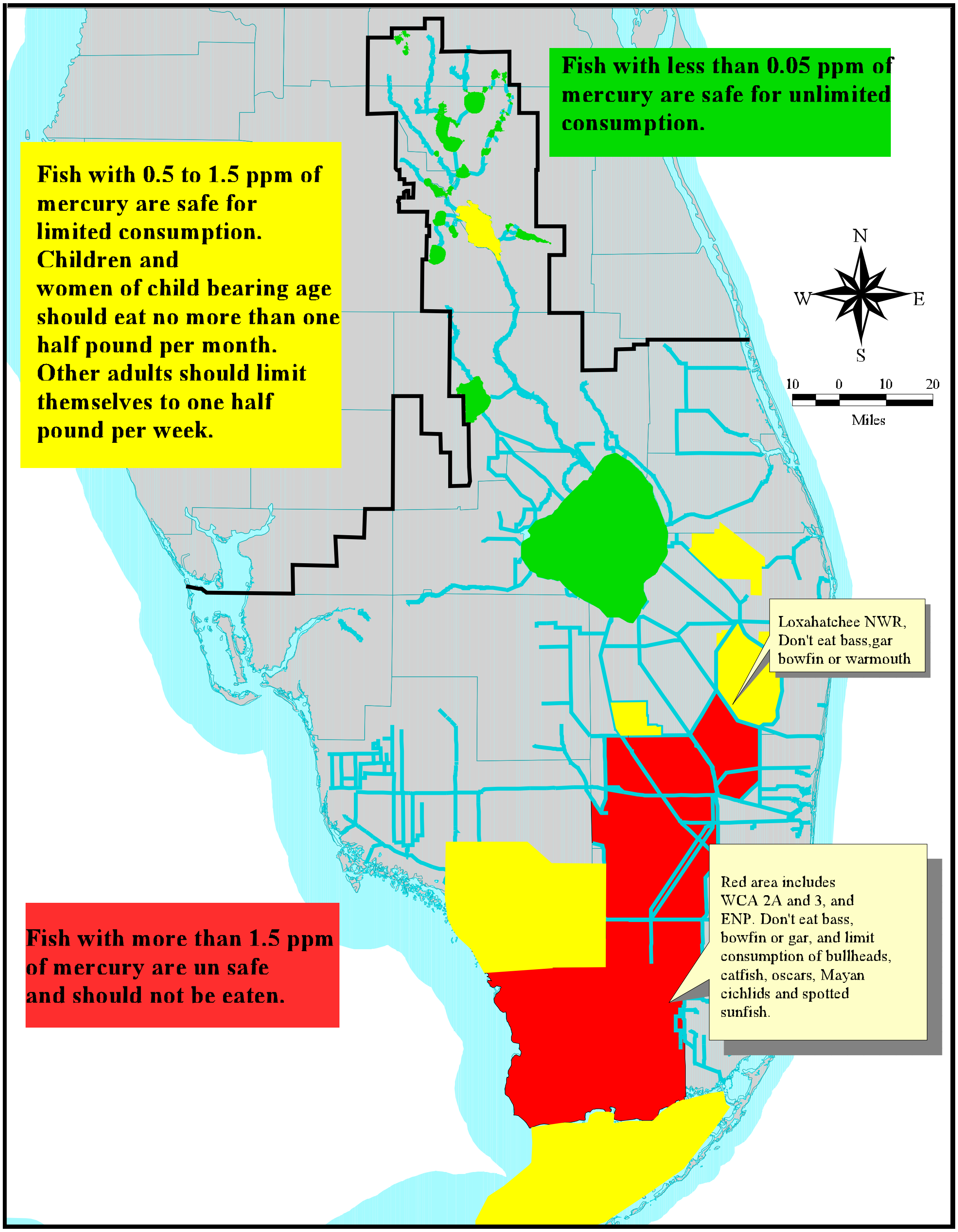


**Figure 7-1.** Mercury fish consumption advisories in Florida.

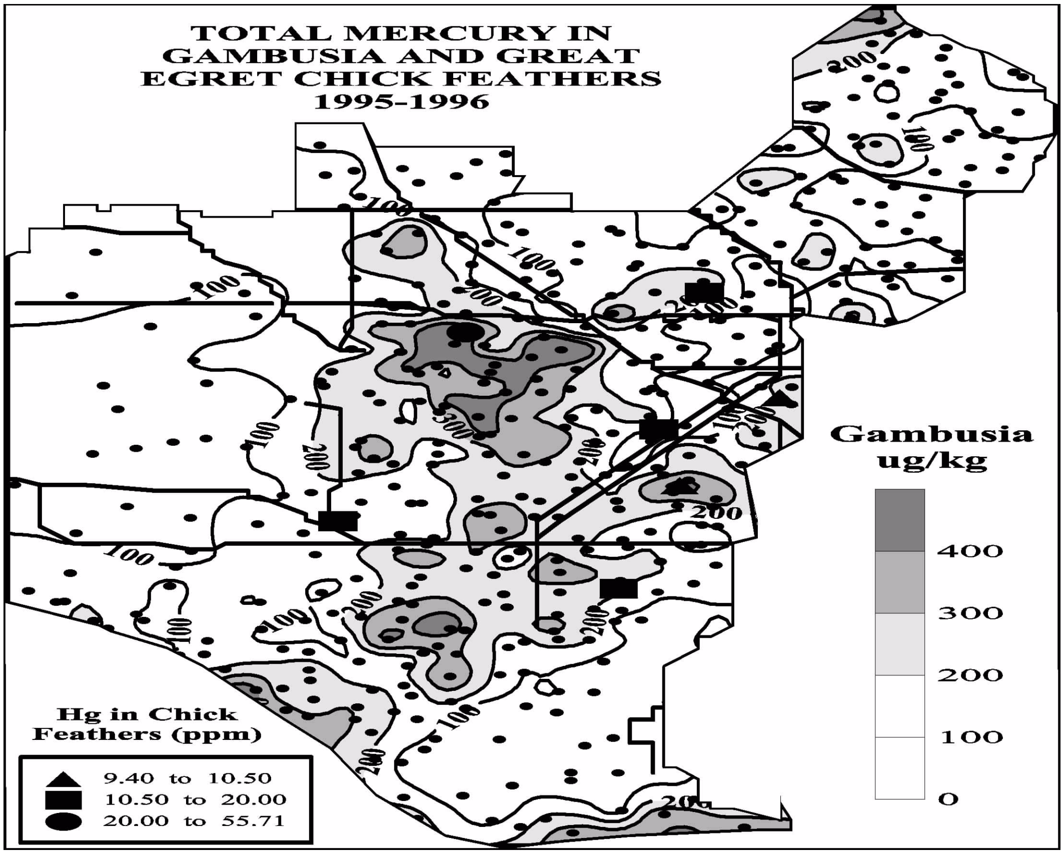


**Figure 7-2.** Distribution of methylmercury contamination in Everglades mosquitofish and wading birds.

Why does the Everglades have a mercury problem? The Everglades is receiving a supply of new inorganic mercury in wet and dry deposition from the air that is roughly twice that in rural Wisconsin. Together with the inorganic mercury present in runoff and peat soil, the inorganic mercury in rainfall is being converted to a very toxic form of organic mercury, methylmercury, by natural bacteria in Everglades peat soil and the thick mats of microscopic one-celled plants called algae. Methylmercury production is believed to be occurring at a higher rate in the Everglades than in any of the other freshwater aquatic ecosystems studied to date. However, the reason for this is not yet completely clear, but high temperature and high sulfate may be key.

Once produced, the methylmercury is distributed among water, sediment and aquatic plants and animals. Methylmercury is readily taken up by plants and animals at the base of the Everglades food chain that graze living and dead plant tissue. These grazers are consumed by primary predator amphibians, crustaceans, and small fish, which are, in turn, consumed by secondary and tertiary predator fish. Methylmercury is readily absorbed, but only slowly eliminated from the bodies of fish. This results in (bio)accumulation of methylmercury in the organs and tissues of the fish. As they grow older and larger, top-predator fish, such as largemouth bass, may bioaccumulate many millions of times the concentrations of methylmercury in the surrounding water. Methylmercury is not toxic to fish-eating wildlife at the levels present in water; however, through this process of biomagnification, it occurs at potentially toxic levels in fish.

The mission of the District's Mercury Studies Program is to provide federal and state agencies with reasonable assuranceof the following:

- There will be no substantial increase in the quantities of total mercury or methylmercury in runoff as a result of the adoption of BMPs by farmers in the EAA.
- The STAs will not cause or contribute to a new mercury problem within their borders or downstream
- The planned reconfiguration of South Florida hydrology to meet the future water supply needs of humans, the Everglades, estuaries, and bays will not cause or contribute to a worsening of the Everglades or Florida Bay mercury problems
- All requirements of federal and state statutes, regulations, standards, and permits governing mercury pollution will be met.

To conduct this mission requires an understanding of the Everglades ecosystem, both pre- and post-restoration, including the following information:

- Supplies of mercury from EAA runoff, peat soil, and air deposition
- Processes that link those supplies to the concentrations of methylmercury in Everglades fish and fish-eating animals
- Influences of water quantity and quality on those processes
- Toxic effects to humans and wildlife when making full use of the Everglades as a sport fishery and wildlife habitat.

The District and DEP continue to support the multi-agency SFMSP to obtain the information and tools needed to understand and solve the Everglades mercury problem.

## PURPOSE OF THIS CHAPTER

This chapter summarizes what is known about the sources, causes, and effects of the existing Everglades mercury problem, and evaluates the likelihood that changes to water quantity or quality to be brought about by the Everglades Construction Project (ECP) or the eventual reconfiguration of the Central and Southern Florida (C&SF) Project will make the existing Everglades mercury problem worse.

During the development of the Everglades Forever Act, the Sugar Cane Growers Cooperative brought to the Legislature its concern that the proposed phosphorus reduction program would make the Everglades mercury problem worse. In adopting the Everglades Forever Act, the Legislature acknowledged that this was unlikely. However, the Legislature also intended that permits issued to the District for the construction and operation of the STAs require mercury monitoring to detect any changes in the Everglades canals or marshes that would indicate otherwise. This would provide ongoing assurances that the phosphorus reduction program would not cause or contribute to a new mercury problem within the STAs or a worsening of the mercury problem downstream. However, the monitoring program would also serve as an early warning system to detect undesirable trends and guide the appropriate response. That monitoring program is now in effect.

The purpose of this chapter is to describe the efforts of the District and DEP to understand and solve the Everglades mercury problem and monitor the Everglades response to the ECP by following the key regulatory steps outlined in the Act:

- Review and evaluate existing data, identify deficiencies and initiate a research and monitoring program to generate such information by January 1996.
- Determine if the existing standard is adequate by December 31, 2001.

- Develop a strategy to revise the standard if inadequate and quantify the links between mercury sources, Everglades water quality, and Everglades mercury responses.
- Submit a permit application by December 31, 2003, embodying a plan for the control of mercury sources and water quantity and quality to meet the revised standard by December 31, 2006.

## CONTENT

Chapter 7 is a summary of the following:

- An assessment of the magnitude, extent, and trends of Everglades contamination, exposures, and risks from total mercury and methylmercury.
- The external conditions and internal characteristics of the Everglades that are causing or contributing to the Everglades mercury problem.
- Options available for reducing methylmercury exposures to fish-eating animals and their predators to acceptable levels throughout the Everglades.
- An analysis of the likely adverse mercury impacts of the various elements of the ECP.
- The next steps for understanding and solving the Everglades mercury problem.

This chapter serves to organize and integrate all of the relevant Everglades mercury monitoring, research, modeling and assessment studies completed to date under the auspices of the SFMSP. It includes a summary of the processes and influential factors that govern the production of methylmercury from the inorganic mercury in rainfall and storm runoff, and as well as that already deposited in peat soil. Such factors include dissolved sulfate, sulfide, and iron in peat pore water and the total mercury in peat soil. Other factors govern methylmercury absorption by microscopic plants, their grazers, and the fish that prey on their grazers, and on up the food chain. Such factors include water column hardness, chloride, dissolved organic carbon (DOC), and total phosphorus in EAA runoff. This is required to provide ongoing assurance to DEP that the ECP will not cause or contribute to a significant increase in methylmercury production or bioaccumulation over time, either within or downstream of the STAs or the Alternative Treatment Technologies (ATTs).

Where appropriate, this chapter summarizes the key issues, findings, conclusions, and recommendations from last year's chapter on the Everglades Mercury Problem, but this chapter excludes the detailed discussion of the environmental physics, chemistry and biology of mercury in the air and water contained in last year's chapter. The reader is referred back to last year's chapter for an introduction to the mercury cycle. In addition, this chapter is not intended to be a review of all of this year's relevant literature on mercury sources, transport, fate, or bioaccumulation outside the Everglades.

## SCOPE

The scope of this chapter includes the lands from which rainfall runs off to the Everglades (watershed), the canals that convey that runoff, and the marshes receiving the canal discharge, as well as the air upwind and above South Florida that carries mercury air pollution over the Everglades (airshed). It has been calculated that EAA runoff contributes less than 5 percent of the new mercury input to the Everglades each year, but it contributes significant quantities of other factors that could influence the mercury cycle. The District is ultimately responsible for managing Everglades water quantity and quality, so this chapter must include mention of those contributions.

The remainder of the new mercury input to the Everglades each year comes from atmospheric deposition. While air source control and air quality monitoring areunder the authority of the USEPA and DEP, the District has a responsibility to report Everglades mercury status and trends revealed through compliance monitoring of STAs and the downstream canals and marshes. Such monitoring is likely to reveal the response of the Everglades to changes in atmospheric deposition from increases or decreases in local, regional, or global sources. It is also the District's responsibility to report on the status and trends of atmospheric deposition to quantify mercury mass contributions outside the District's control. Consequently, this chapter also includes a summary of the results of air emissions, plume transport and modeling studies that are otherwise outside the District's purview for study or control.

Although Florida Bay is not strictly a component of the Everglades, the use of its sport fishery has also been impaired by excessive mercury levels. Like the Everglades, mercury is being supplied to Florida Bay in atmospheric deposition and release from contaminated sediments, as well as Everglades flow through Taylor Slough; however, the relative proportions of these contributors may be quite different. Solving the Everglades mercury problem, while restoring higher freshwater flows to Florida Bay, may benefit the sport fishery in Florida Bay. Therefore, it is appropriate to include Florida Bay in the discussion of the Everglades mercury problem and its solution.

## ORGANIZATION

The core content of this chapter is organized around six key management questions that are intended to guide the design of the relevant Everglades studies for the support of timely, scientifically credible, and legally defensible Everglades restoration decision-making. These questions are as follows:

- What is the significance of the Everglades mercury problem?
- Can the control of local sources reduce Everglades mercury risks?
- Can the management of water quantity or quality reduce Everglades mercury risks?
- How will South Florida restoration efforts affect Everglades mercury risks?
- What tools are required to understand and solve the Everglades mercury problem?
- What is the status of District and DEP efforts to meet Act mercury mandates?

Following the Summary and Introduction, the Background begins with an overview of the general mercury problem worldwide, and then focuses on the Everglades mercury problem and the SFMSP created to understand and solve it. This is followed by a summary of the joint District-DEP Everglades Mercury Action Strategy that outlines a process for fulfilling the mercury mandates of the Act over the next five years. The chapter then provides an Update on the Answers to the Six Key Everglades Mercury Management Questions to the extent permitted by the cumulative scientific understanding and modeling results to date. The chapter closes with a Summary of the Key Findings, Conclusions, and Recommendations.

This chapter is organized so that it is of interest to both a general reader and a technical reader. At appropriate junctures, the text in the main body of the chapter refers the reader to the appendices for the technical detail supporting the summary of key findings, conclusions, and recommendations. The appendices include the following:

- Everglades Mercury Action Strategy;
- Mercury compliance report that meets all requirements of applicable statutes and permits;
- Update on mercury contamination trends in wading birds and to last year's post-STA ecological risk assessment for methylmercury toxicity to wading birds using new data and advanced techniques;
- Analysis of adequacy of existing Class III Water Quality Standard for total mercury to protect Florida panther;

- Five-year summary of ENR Project mercury studies; and
- Recommended Phase 2 research initiatives to close critical data gaps.

## WHY IS MERCURY A GLOBAL AND NATIONAL PROBLEM?

Methylmercury accumulates in the organs and tissues of the body and, unlike the organochlorine pesticides, has a higher affinity for protein than fat (WHO, 1976). Methylmercury crosses the brain barrier in all higher animals and the placental barrier in mammals (WHO, 1976). Once present in the fetus, methylmercury interferes with brain and nervous system development (Clarkson, 1994). Depending on the amount of methylmercury that has been transferred to or accumulated in the fetus, methylmercury can cause mild to severe retardation, twisted extremities, and even death (WHO, 1976). Depending on the amount of methylmercury that has been transferred to and accumulated in the brain, in higher animals a progression of symptoms occurs, from subtle losses in problem-solving skills and visual acuity to numbness of the lips, face, and extremities to tremors, vomiting, paralysis and death (WHO, 1976; USEPA, 1980). The extreme effects of methylmercury in humans is referred to as Minamata Disease, after the city in Japan where such effects in aborted fetuses, stillborns, newborns, children, and adults were first documented in the mid-1950s through the mid-1960s (Ehrlich et al., 1977). However, the fish advisories are set to prevent the occurrence of even the most subtle toxic effects from methylmercury, so individuals consuming large quantities of fish from the Everglades are highly unlikely to experience some of the more mild symptoms of methylmercury posioning, let alone the extreme effects of Minimata Disease.

Mercury is present in a number of common items, including silent switches, fluorescent lights, thermometers, and batteries (USEPA, 1997). When these items are thrown away with household or commercial refuse, they can be burned with other refuse in a municipal waste incinerator, releasing the mercury back to the environment. However, a number of states have initiated voluntary or mandatory mercury reduction programs for municipal waste incinerator feedstocks. Florida's Environmental Regulation Commission passed such rules in 1993. USEPA is now negotiating voluntary source reduction agreements with the medical waste incinerator industry (Alexis Cain, USEPA, personal communication, 1999). To reduce mercury emissions, some crematoria are now routinely extracting the mercury dental fillings of the deceased prior to cremation. Mercury discharges to surface waters from chlor-alkali manufacturing facilities have been generally greatly curtailed, but runoff from uncontrolled waste disposal sites of industrial wastes may still be a significant source in some locations (USEPA, 1997). Inorganic mercury salts can still be used as a seed fungicide, but the use of methylmercury as a seed fungicide has been banned and its use as a fungicide for treating ornamental sod severely limited (USEPA, 1997).

Methylmercury and a related compound, dimethylmercury, are also produced naturally from the inorganic mercury present in watershed runoff, atmospheric deposition and groundwater discharge by bacteria in sediments under conditions devoid of dissolved oxygen (Jensen and Jernelov, 1969; Beijer and Jernelov, 1979). More recently, methylmercury production has been demonstrated in the thick mats made up of one-celled plants called algae (Cleckner et al., 1999). Methylmercury predominates over dimethylmercury production in aquatic sediments or hydrated soils (Fitzgerald, 1989), but dimethylmercury is a substantial contaminant of unflared landfill gas (S. Lindberg, ORNL, personal communication, 1999). Once produced, methylmercury is readily absorbed but only slowly eliminated by fish (Norstrom et al., 1976). In all but the smallest fish, most methylmercury absorption is from food rather than directly from the water. This results in a phenomenon referred to as bioaccumulation. The ratio of the methylmercury concentration in a fish to the concentration in the surrounding water is its bioaccumulation factor (BAF). Fish will bioaccumulate higher concentrations of methylmercury than what they feed on (Rodgers, 1994). This results in a phenomenon referred to as biomagnification, which occurs at each successive step in the aquatic food chain (Wood, 1974). In general, small, short-lived fish at the lowest trophic level exhibit BAFs in the range of 10,000-100,000, their larger, longer-lived predators exhibit BAFs in the range 100,000-1,000,000, and for top-predator fish like largemouth bass, BAFs in the range 1,000,000-10,000,000 are not uncommon (Watras, 1993). For example, in the most contaminated portion of the Everglades in WCA-3A, the BAF for a three-year old largemouth bass can approach 10,000,000 (Lange et al., 1998). Without such high BAFs, methylmercury would not be a problem in the Everglades and elsewhere.

To put the Everglades mercury problem in context and perspective, the U.S. has a mercury problem, with at least 40 states having issued fish consumption health advisories for mercury-contaminated waters (USEPA, 1997). Florida has a statewide mercury problem, with more than 50 percent of its inland waters now under Health Department advisories for limited or no fish consumption because of mercury. Sport fish from the Everglades canals and marshes have the highest mercury concentrations in the state (Lange et al., 1999). The area covered by the Florida advisories may be the largest in the U.S. (T. Atkeson, DEP, personal communication, 1996).

The Everglades appears to be especially susceptible to a methylmercury problem, and much has been learned as to why this is the case. The rate of inorganic mercury deposition to the Everglades (Guentzel et al., 1997) is twice that of rural Wisconsin (Benoit et al., 1994). The inorganic mercury deposited on the water's surface is diluted by only slowly flowing water. The Everglades never freezes, and its waters are warmer than 25°C for at least six months per year, so the metabolisms of bacteria, aquatic plants, and animals are accelerated. The activity of the sulfate-reducing bacteria involved in methylmercury production may be accelerated in the northern and central portions of the remnant Everglades due to the presence of excess sulfate. Finally, the Everglades has a very large surface area and a very slow flow rate, so the methylmercury produced is only slowly diluted by flowing water.

However, uncertainties remain regarding several scientific issues, including the issues below:

- The contributions of local air pollution sources versus the worldwide background to the fresh supply of inorganic mercury to the Everglades each year.
- The importance of the path the inorganic mercury takes in filtering through the aquatic ecosystem to its short- and long-term storage depots and the speed with which this occurs.
- The fraction of the inorganic mercury in the algae mat and peat soil that is in a form that can be taken up by sulfate-reducing bacteria for methylation, and the conditions and factors that influence the magnitudes of those fractions.
- The fraction of the methylmercury that is actually available for demethylation by other communities of bacteria, the fraction that is absorbed by one-celled plants, the fraction that is complexed with dissolved organic matter, and the conditions and factors that influence the magnitudes of those fractions.
- The typical diets of potentially highly exposed animals (for example, the otter and mink) and the effects of vegetation types and densities, water depth, and water quality on feeding behavior.

Despite the great advances in understanding achieved to date, clearly much remains to be learned before the responsible agencies can develop the optimum solution to the Everglades mercury problem. This is the challenge faced by the SFMSP over the next three years.

## THE SOUTH FLORIDA MERCURY SCIENCE PROGRAM

The adaptive management strategy for understanding and solving the Everglades mercury problem has been developed and implemented under the aegis of SFMSP, an informal partnership of federal, state and local agencies and private entities committed to conducting the studies required to understand and solve the South Florida mercury problem. In addition to the DEP and District, the partnership consists of the Florida Game and Wildlife Conservation Commission (FGWCC), the U.S. Geological Survey (USGS), the U.S. Environmental Protection Agency (USEPA), the National Oceanic and Atmospheric Administration (NOAA), the U.S. Army Corps of Engineers (Corps), the Wisconsin Department of Natural Resources (WDNR) and the Electric Power Research Institute, the Florida Electric Power Coordinating Group, including the Southern Company, and Florida Power & Light Company. Research institutions funded for this effort include Florida International University, the University of Florida, Florida State University, the University of Michigan-Ann Arbor, the University of Wisconsin-Madison, the Department of Energy's Oak Ridge National Laboratory in Oak Ridge, Tennessee and the Academy of Natural Science's Estuarine Research Laboratory in St. Leonard, Maryland. Students from the Massachusetts Institute of Technology have also conducted Everglades mercury research with in-kind District support. The multi-agency and entity effort is being coordinated by the Science Program Management Committee, composed of representatives of each of the participating agencies in Florida.

The scientific objectives of the SFMSP are to identify, characterize and quantify:

- Mercury sources, including farm and urban runoff, wet deposition of dissolved inorganic mercury in rainfall and dry deposition of reactive gaseous mercury salts.
- Pathways that bring mercury into (inputs) and remove mercury from (outputs) the Everglades and the short- and long-term storage depots like vegetation and soil.
- Interrelated processes that translate the inorganic mercury supply into methylmercury contamination and the factors and conditions that influence their routes and rates.
- Magnitude, extent and duration of existing mercury contamination in the Everglades ecosystem and the rates at which short- and long-term storage depots will clear themselves when inorganic mercury sources are reduced to acceptable emissions levels.
- Magnitude of uptake, disposition, accumulation and toxic effects in humans and wildlife from the consumption of contaminated food, and the rates at which short- and long-term storage depots within the body will clear themselves when methymercury concentrations in food are reduced to acceptable levels.

The results of the required studies will be translated into a quantitative predictive capability in the form of a mathematical model. The model will be used to evaluate the response of the Everglades to various mercury source reduction scenarios under conditions of water quantity and quality brought about by the ECP or the C&SF Comprehensive Review Study (Restudy). To the extent practicable, the mercury studies required to achieve these objectives have been planned and coordinated with related, concurrent meteorological, hydrological, water chemistry, and nutrient studies being conducted in South Florida by various public and private entities. This is intended to ensure comparability of results, to avoid duplication of effort, and to cut costs.

The data generated in the required studies are organized, analyzed and integrated to support restoration decision-making based on a risk management approach. The strategy for developing the required understanding and tools is an adaptive process based on a phased approach to study design, data interpretation, and management decision-making. In this adaptive process, the program objectives and allocation of monitoring, research, modeling, and assessment resources are reviewed periodically and modified as appropriate in response to what has been learned to that point. The periodic review process is facilitated by rapid dissemination of study results to the principal investigators and program managers at annual workshops with biennial peer review. The preparation of an annual, peer-reviewed synthesis report translates recent key scientific findings and modeling results into key conclusions and recommendations to guide resource management decision-making by the responsible senior officials. This year's Chapter 7 of the Everglades Consolidated Report serves as that annual synthesis report.

The monitoring, research, modeling and assessment studies of the SFMSP are to be conducted in phases. The SFMSP Phase 1 studies adapted existing methods of mercury monitoring and research to the Everglades environment, quantified the major pathways of mercury addition to the Everglades, mapped the mercury contamination of the Everglades and identified the key processes, factors and conditions that are most likely to govern methylmercury production and bioaccumulation. The results of the Phase 1 studies have been organized and integrated within the framework of a first generation mechanistic model of mercury cycling and bioaccumulation in the Everglades ecosystem. Phase 1 was completed in 1998.

In addition to its utility in guiding the development of the research program and in properly interpreting disparate research results, the model has immediate utility for the Everglades restoration program. To date, the model has been used to predict Everglades mercury responses to various proposed changes in water quantity and quality. The results of these modeling exercises were used in the preparation of the application for the STAs, in the Programmatic Environmental Impact Statement for the Restudy. Subsequently, the model was used in the evaluation of the interim and final Restudy water management scenarios.

SFMSP Phase 2 studies will focus on quantifying the most significant mercury sources, the most significant mercury cycling processes and the most significant mercury exposures and toxic effects in the Everglades. Phase 2 study results will be used to produce a Phase 2 model with which to generate more accurate, precise and reliable predictions of the effects of various mercury source reduction options under post-ECP or post-Restudy conditions. In Chapter 7 of last year's Everglades Interim Report, the District was able to demonstrate that the known benefits to the Everglades from phosphorus reduction would outweigh its potential mercury detriments, should they occur at all. It is unlikely that the results of the Phase 2 studies or the refined Phase 2 model predictions will reverse this conclusion.

# EVERGLADES MERCURY ACTION STRATEGY

## OBJECTIVES AND APPROACH

The objectives of Everglades Mercury Action Strategy (E-MAS) are to restore full uses of the Everglades, protect human health and wildlife, and prevent any significant post-restoration adverse impacts. The mercury recovery process envisioned by the District, DEP and USEPA for the Everglades includes five elements:

1. Development of a restoration target in the form of a water, sediment or fish quality criterion that ensures unimpaired use and protection of wildlife, including the alligator, the endangered wood stork and the Florida panther.
2. Further development and application of an existing model that relates the total mercury loading rate to corresponding methylmercury concentrations in water, sediment and fish under low flow and stage conditions with an ample margin of safety.
3. Application of an existing model that relates reactive gaseous mercury air emissions rates to the corresponding wet and dry deposition rates on the Everglades.
4. Development and implementation of local source emissions reduction targets corresponding to the attainment and maintenance of the restoration quality targets.
5. Quantification of nonabatable sources that preclude the attainment and maintenance of the target restoration criteria at this time.

## RESTORATION TARGET DEVELOPMENT AND APPLICATION

USEPA is already in the process of developing a new Water Quality Criterion (WQC) to protect human health. The District, DEP and the USGS have begun to develop a joint study plan to close the science gaps that preclude the development of a total mercury WQC to protect Everglades wildlife. DEP will then develop site-specific alternative criteria (SSAC) for human health and wildlife as needed for direct application to the Everglades. The more protective of the Everglades SSAC for human health or wildlife will then become the basis for the reduction in the new mercury load entering the Everglades each year.

## MODEL DEVELOPMENT AND APPLICATION

The District, DEP and the USEPA continue to fund the enhancement of the first generation of the Everglades Mercury Cycling Model (EMCM-1) with which to predict post-ECP and post-Restudy mercury risks to wildlife. The model and its applications were described in Appendix 7-4 of last year's Everglades Interim Report (Ambrose and Araujo, 1999). The proposed model refinements are intended to decrease the uncertainty in estimated post-restoration methylmercury concentrations and increase the confidence in the results of the District's post-ECP ecological risk assessment, which was based on a reference site approach (Appendix 7-2 of last year's Everglades Interim Report; Rumbold et al., 1999). In particular, addition of equations that link the mercury and sulfur cycles will permit the evaluation of the benefits and detriments of various scenarios for the reduction of sulfur application rates on sugar cane farm soils. An existing wetlands aquatic fate model will be used to calculate the capacity of the Everglades to assimilate the new mercury load so as not to exceed the target SSAC under appropriate low flow conditions and to provide the ample margin of safety required by the Clean Water Act. This is its total maximum daily load (TMDL). An air source model will then be used to guide the reduction of local air emissions sources to meet the SSAC, if possible.

## NONABATABLE SOURCES

There are two potentially significant non-abatable sources of inorganic mercury to the Everglades. The first is the inorganic mercury reservoir in the peat soil underlying the Everglades, which is three to six times more contaminated than in the late 1800s. The second is the atmospheric deposition fed by the global background that occurs even when the wind is blowing out of the west, carrying mercury emissions from local sources out over the ocean rather than the Everglades. If non-abatable sources of inorganic mercury preclude the attainment of the SSAC at this time, a temporary variance from the SSAC will be requested by the District, while DEP evaluates the option of manipulating water quantity and quality to reduce the rate of release and methylation of inorganic mercury from the underlying peat soil. However, this is not a preferred option. In this case, the preferred option is the negotiation of a global source reduction treaty for mercury under the aegis of the Department of State and the guidance of the USEPA, but which is outside the purview of either the District or DEP.

## TIMELINES AND COSTS

The target date for promulgating the SSAC and the issuance of source control permits to meet it is no later than December 31, 2003, to attain and maintain compliance with the SSAC by December 31, 2006. Over the next five years, approximately \$2.5 million in District funds, \$4 million in DEP funds, and about \$10 million in combined USGS and USEPA funds are expected to be spent on the research, modeling and criteria development to support the solution to the Everglades mercury problem, pending budget approval by their respective governing bodies. This should increase the likelihood that the target dates in the Act are met and that the Everglades responds as expected to source reduction measures over an appropriate time period, taking into account the contributions from non-abatable sources.

# WHAT IS THE SIGNIFICANCE OF THE EVERGLADES MERCURY PROBLEM?

## SUMMARY

The mercury problem remains significant throughout most of the Everglades, as evidenced by the continuation of the sport fish consumption advisories issued by the Department of Health. In addition, some fish-eating animals or their predators may be at an unacceptable risk of methylmercury toxicity in some locations. While the use of the sport fishery has been impaired, the numerical Class III Water Quality Standard of 12 ng/L is not being routinely exceeded anywhere in South Florida. DEP has concluded that the existing standard is inadequate to protect the resource. However, the concentrations of total mercury in largemouth bass and great egrets appear to have declined at several northern and central Everglades locations over the last five years. Corresponding data for the Florida panther are unavailable as of this writing, although there are anecdotal reports of significant declines. If this trend continues, the existing fish advisories may have to be revised. DEP reports that mercury emissions from municipal incinerators in South Florida have decreased by about 65 percent over the last five years in response to rules passed by the Environmental Regulation Commission in 1993 requiring reduction of mercury in waste feedstocks. However, the U.S. background may have begun to decrease as much as 20 to 40 years ago, so further study is required to determine the cause of the apparent declines. Those studies are taken up in the answer to the next key management question.

To address the question of significance, one must consider the nature of the problem, its magnitude, extent, duration and frequency of recurrence, and the socioeconomic or administrative significance of the species affected. The answers to the following questions are provided in the following subsections:

- What are the benchmarks that determine the environmental significance of mercury contamination?
- What are the magnitude, extent and persistence of mercury contamination in water, rainfall, sediment and wildlife measured relative to these benchmarks?
- What are the trends in mercury contamination over the last decade?
- Are the existing benchmarks adequate to protect the uses, ecological integrity and endangered species in the Everglades?

## BENCHMARKS OF ENVIRONMENTAL SIGNIFICANCE

The environmental significance of the Everglades mercury problem is quantified in terms of the magnitude, spatial extent and persistence of methylmercury contamination that has one or more of the following effects:

- Impairs the use of the Everglades as a sport fishery;
- Significantly reduces the reproductive success of highly exposed aquatic or terrestrial wildlife populations; and
- Significantly reduces the health of individual members of trust species populations.

One of the Everglades ecological restoration objectives set by the South Florida Ecosystem Restoration Task Force is to protect highly exposed carnivores species like the alligator, wood stork, and Florida panther from significant mercury toxic effects (Federal Task Force, 1997). However, these criteria have not yet been translated into equivalent mercury concentrations in the preferred prey of these indicator species or the water, sediment or vegetation in which these preferred prey live.

Although studies of human exposure and effects have been conducted, the accepted benchmarks of significance from a human health standpoint are the action levels for issuing a limited consumption fish advisory or a no consumption fish advisory. For humans, Florida protects the public health by issuing sport fish consumption advisories. No fish consumption is recommended for anybody when mercury concentrations in edible flesh exceed 1.5 ppm in the flesh of largemouth bass standardized to age class 3 years. No more than one, eight-ounce meal a week is recommended for healthy males and no more than one, eight-ounce meal a month is recommended for women of child-bearing age and children when concentrations are between 0.5 ppm and 1.5 ppm. Below 0.5 ppm unlimited consumption is permissible for everyone. To protect fish-eating fish from the toxic effects o methylmercury, Florida has adopted the numerical Class III Water Quality Criterion for total mercury in surface water recommended by USEPA of 12 parts per trillion (nanograms per liter or ng/L).

For the protection of aquatic life and human health, Florida has adopted the numerical Class III Water Quality Criterion for total mercury of 12 ng/L. Florida has not yet adopted a total mercury Water Quality Criterion for the protection of fish-eating wildlife based on methylmercury toxicity and exposure via the food chain. USEPA has not yet published National Water Quality Criteria for total mercury to protect fish-eating wildlife from methylmercury toxicity, but USEPA has published a proposed set of regional numerical total mercury Water Quality Criteria to protect Great Lakes wildlife (FR April 16, 1993, Part 2. 40CFR Parts 122 et al.). For the protection of fish-eating mammals, 1.6 ng/L is derived, and for the protection of fish-eating birds, 1.3 ng/L is derived (USEPA, 1993). Using the same approach and methylmercury no observable adverse effect levels, but substituting appropriate Everglades for Great Lakes fish bioaccumulation factors, the equivalent concentrations for the WCA-3A-15 in the Everglades are 0.2 ng/L to protect fish-eating birds and 0.4 ng/L to protect fish-eating mammals.

In its Mercury Report to Congress, USEPA proposed that total mercury in fish not exceed 0.3 parts per million (ppm or mg/Kg) to protect fish-eating birds (USEPA, 1997). This proposal has not yet been formalized, however. Following the same approach used for the derivation of the total mercury Water Quality Criterion for the Great Lakes Initiative, the equivalent concentration in trophic level 3 and 4 fish in the Everglades would be 0.04 and 0.14 mg/Kg, respectively. No sediment quality criteria exist for total mercury or methylmercury at present, but it might be possible to derive them in terms of the acid volatile sulfide fraction or the chromate oxidizable sulfide fraction in Everglades hydrated peat soil.

## WATER

The status and trends in canal water quality are summarized in **Appendix 7-2** for quarterly samples collected at 10 District structures. There were no exceedances of the numerical Class III Water Quality Standard of 12 ng/L at any location at any time. Nor were there any discernible time trends in the concentrations of total mercury or methylmercury at any of the ten sites over the first two years of monitoring, but a pattern has emerged that merits acknowledgment. Higher total mercury and methylmercury concentrations tended to occur during the rainy season, when the corresponding concentrations of total mercury and rainfall quantities are at a maximum, and lower total mercury and methylmercury concentrations tended to occur in the dry season, when the corresponding concentrations of total mercury and rainfall quantities are at a minimum. The federal and state permits for the operation of the STAs and Everglades structures do not require monitoring for total mercury and methylmercury in water at the interior marsh compliance sites, because the marsh water column concentrations are highly variable, responding to immediately antecedent meteorological conditions and time of day (Krabbenhoft et al., 1998), among other factors. Instead, fish and wading birds were believed to be more reliable spatial and temporal integrators of the bioavailable methylmercury concentration in the aquatic environment than the filtered methylmercury concentration in the water column (P. Parks, DEP, personal communication, 1997).

## FISH

The choice of an appropriate aquatic species for mercury monitoring must take into account its place in the food web, its foraging preferences, its cultural and ecological importance and its availability. Compliance and research monitoring of mercury concentrations in fish continue to focus on largemouth bass (*Micropterus salmoides*), sunfish (*Lepomis spp.*) and mosquitofish (*Gambusia holbrooki*). Largemouth bass and sunfish are sport fish of cultural interest and are therefore monitored to ensure the protection of human health. Feeding studies indicate that sunfish make up an important portion of the diet of various wading birds (Frederick et al., 1997; Ogden et al., 1978) and are monitored to help estimate the level of mercury exposure to these organisms. Mosquitofish, an opportunistic omnivore, are not important in the diets of wading birds (Frederick et al., 1997; Ogden et al., 1978), nor do they make up significant portions of the diet of sunfish or largemouth bass (Loftus et al., 1998; Lange et al., 1998). Nevertheless, mosquitofish are ubiquitous, ensuring availability and comparability of data throughout South Florida. Due to their ubiquity, in the absence of other data, mosquitofish have been used as a surrogate for fish that are included in the bass or wading bird diets.

**Figure 7-3** depicts the total mercury concentrations in mosquitofish, sunfish and largemouth bass collected during compliance monitoring at the 12 interior marsh sites in the fall of 1998. Over the last decade, there is some evidence of a downward trend of methylmercury in largemouth bass standardized to age class three years at some locations

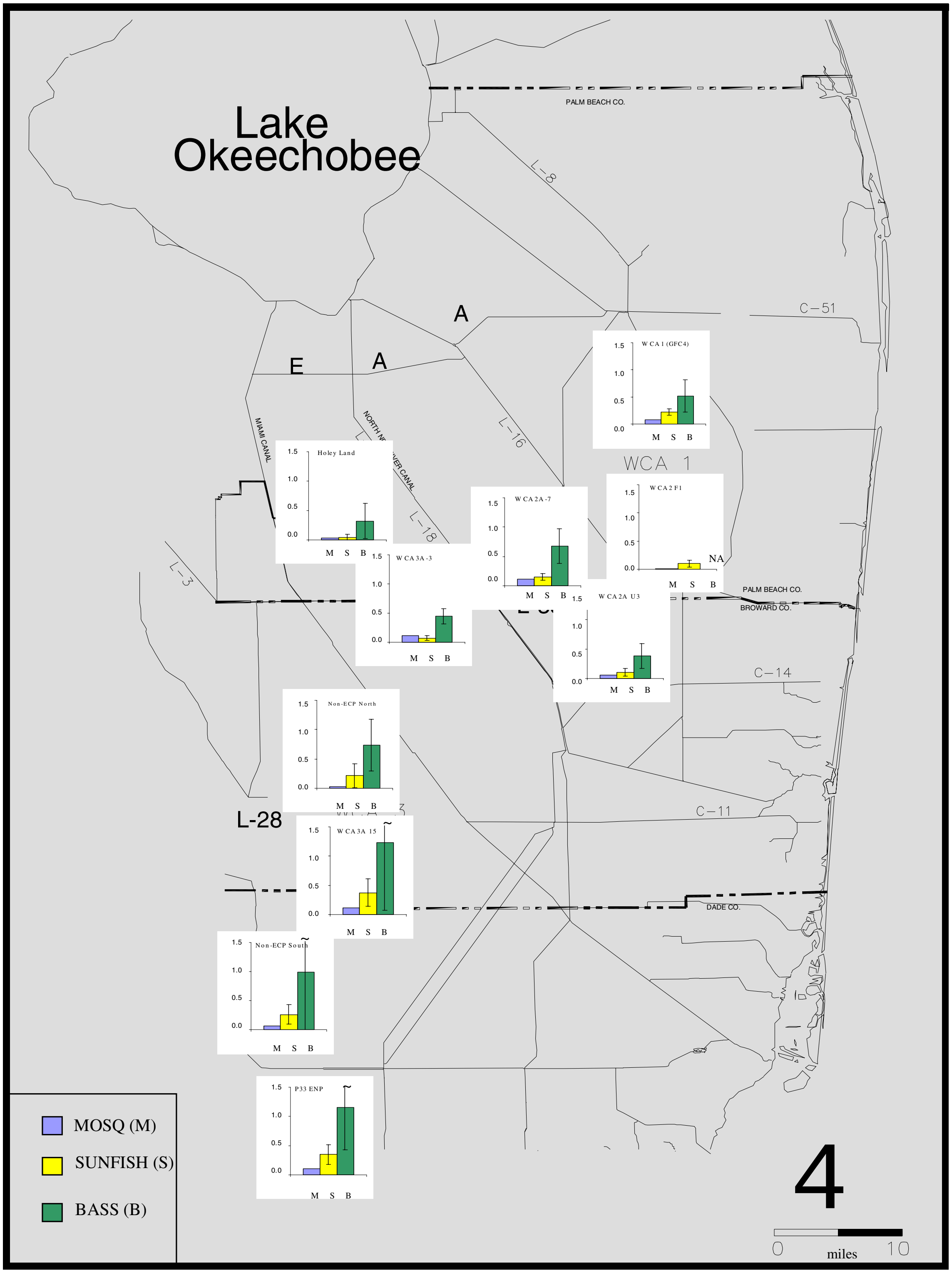


**Figure 7-3.** South Florida spatial trends in total mercury in mosquitofish, sunfish and largemouth bass for 1998.

in South Florida (Lange et al., 1999), including the ENR Project, WCA-1 interior, WCA-2A interior, the L-67 canal and the northern portion of the Park (**Figure 7-4**). If this trend continues, WCA-2A could be upgraded from a no-consumption to a limited-consumption advisory, while WCA-1 could then be upgraded from a limited-consumption to an unlimited-consumption advisory. However, new epidemiological data obtained by USEPA from studies of human populations living on islands where fish consumption rates are high suggest that the present methylmercury no observable adverse effect level in humans may be overprotective or underprotective (A. Kuzmack, USEPA, personal communication, 1999). If a change in the present value of 0.1 microgram per kilogram of body weight per day (0.1 ug/Kg-day) is adopted, this could have ramifications for Florida's fish consumption action level and its Water Quality Criterion to protect human health.

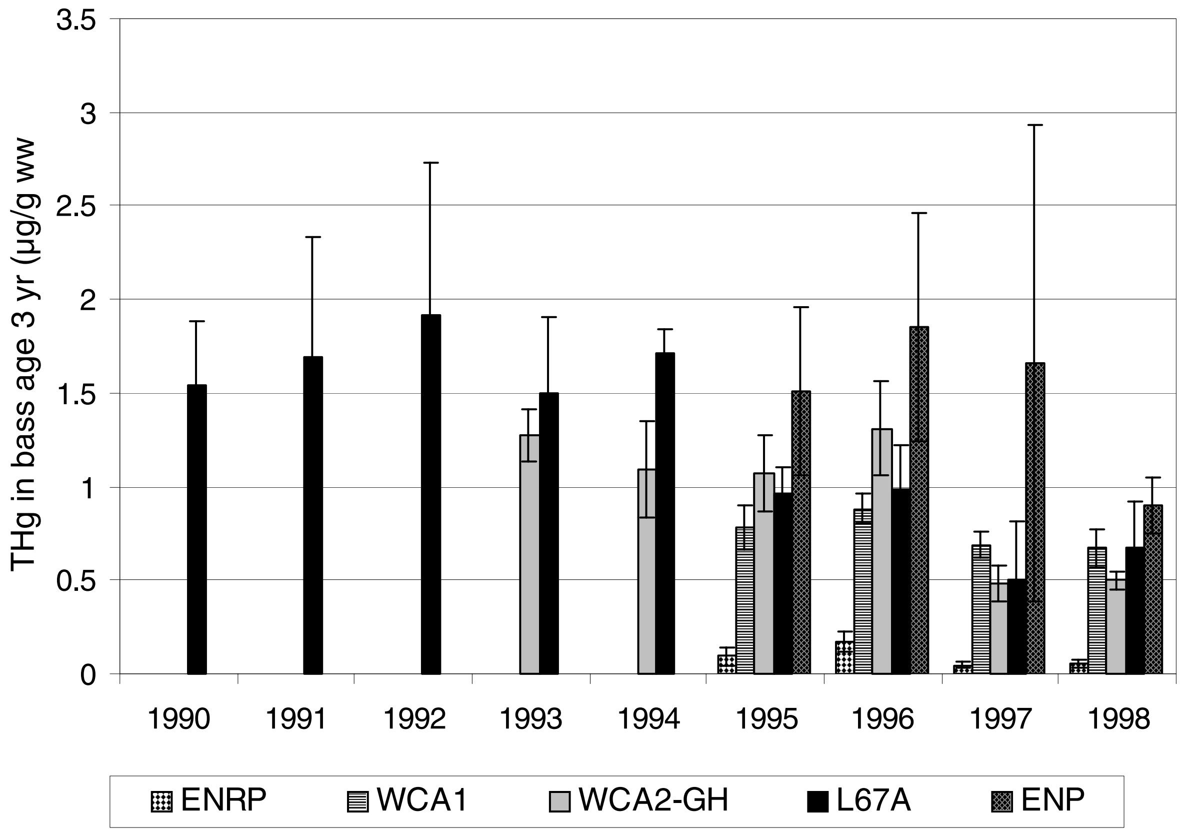


**Figure 7-4.** Total mercury in South Florida largemouth bass over time.

## WADING BIRDS

### Forage Contamination Status and Trends.

Wading birds forage over large areas in search of preferred prey in size classes appropriate to their size, bill shape, throat diameter, and feeding style. A few species of Everglades fish-eating birds spear their prey, which allows them to catch and consume fish larger than their throat diameter by tearing the flesh prior to swallowing. The rest tend to consume their prey whole.

Wood storks feed primarily on small fish in the size range of 2.5 to 10 cm, but can ingest fish as large as 25 cm, and, due to their feeding style, may ingest some benthic invertebrates and sediment incidentally (Ogden et al., 1978). The great egret feeds on a variety of aquatic life in the size range 2.5 to 17 cm, including crayfish, sunfish species (e.g., redear, pumpkinseed, and bluegill), and juvenile bass, and on a variety of terrestrial life, including frogs, snakes, and lizards, depending on availability. Great blue herons feed primarily on larger fish in the size range 5 to 25 cm length (USEPA, 1993), but it is possible that fish as large as 30 cm in length could be ingested (Ryder, 1950). In the Everglades, these size preferences may include sunfish and tilapia species and juvenile warmouth, largemouth bass, and gar.

Mercury concentrations tend to increase with the size and age of each fish species. As a consequence, the quantification the status and trends of mercury residues in the prey fish species of fish-eating birds is more complicated than for humans. Nevertheless, it would appear appropriate to determine whether the apparent trend in age class 3-year standardized bass collected at several locations in the Everglades canals and marshes is also occurring in species of fish in the size class routinely taken by wading birds. To obtain sufficient data for trend analysis, the L-67 canal monitoring site was selected, where fish have been collected continuously since 1991 (Ware et al., 1991). Even then, it was necessary to group the years together to ensure that the population sample size was sufficient. For purposes of this analysis, the wood stork feeding size limit of 250 mm was used as a reference. The results of the one way analysis of variance indicates that there is a significant downward trend in juvenile largemouth bass concentration of total mercury, from a mean of 1.2 mg/Kg wet weight in 1991/92 (S.D. ±0.476) to a mean of 0.3 (S.D. ±0.21), with each paired set of years demonstrating a significant difference ($p < 0.001$). Using the pairwise multiple comparison procedure (Tukey Test), 91/92 and 97/98 were found to be significantly different. It can be concluded that the downward trends observed in age class 3-year standardized largemouth bass at other canal and interior marsh sites (e.g., L-7, WCA-2A-U3 and ENP-PP) are also occurring in the juvenile bass. It may be that the juvenile bass are responding even more rapidly to the environmental changes than their older and larger relatives, because they are probably taking in less contaminated prey, experiencing more rapid growth with associated growth dilution and excreting methylmerury at a higher rate, because the depuration rate coefficient in fish tends to increase with decreasing size (Norstrom et al., 1976).

### Population Contamination Status and Trends

Wading birds are exposed to methylmercury concentrations by consuming fish present in their feeding ranges. The quantity of methylmercury that accumulates in each wading bird reflects the difference between what it has taken up through feeding and what it has lost through excretion, deposited in growing feathers or deposited in eggs. Some of the methylmercury is converted to inorganic mercury inside the body, so the quantity of mercury present in the body is best expressed in terms of a total mercury body burden. Both methylmercury and inorganic mercury are only slowly eliminated form the body, which explains the high total mercury residue levels in the birds feeding on methylmercury-contaminated fish. The half-life in the bird's body is about one to two months (Frederick et al., 1997). As a result, the total mercury concentration in each wading bird represents a spatial average of the concentrations of methylmercury in the fish that it ate over the previous six half-lives, or between six and 12 months. Changes in the average concentrations of total mercury in the tissues, feathers, or eggs of wading bird populations are thus more representative of long-term, large-scale changes in the environment in which they feed than to short-term, localized changes. This is extremely valuable information when tracking the contamination status and trends of the Everglades as a whole.

The federal and state permits issued to the District for the construction and operation of or discharge from the STAs include a requirement to monitor mercury residues in interior marsh great egret populations at two highly contaminated colonies in WCA-3A. These populations have been under study for about a decade, and mercury residue data have been collected since the early 1990s. The District collected the first feather and egg samples from these colonies in March and April of 1999. These new results for total mercury in great egret feathers from chicks were age-standardized to a standard bill length (7.1 cm) using the regression relationship developed by Frederick et al. (1997) and compared to previous results from these colonies. The results of the analysis of total mercury in 20 eggs collected from those same WCA-3A colonies were compared to data previously obtained by Dan Day (personal communication). As with the largemouth bass, there is now the suggestion of a downward trend in total mercury concentrations in both feathers and eggs over the last five years, as depicted in **Figure 7-5**. The analysis of these data is presented in some detail in **Appendix 7-3a**.

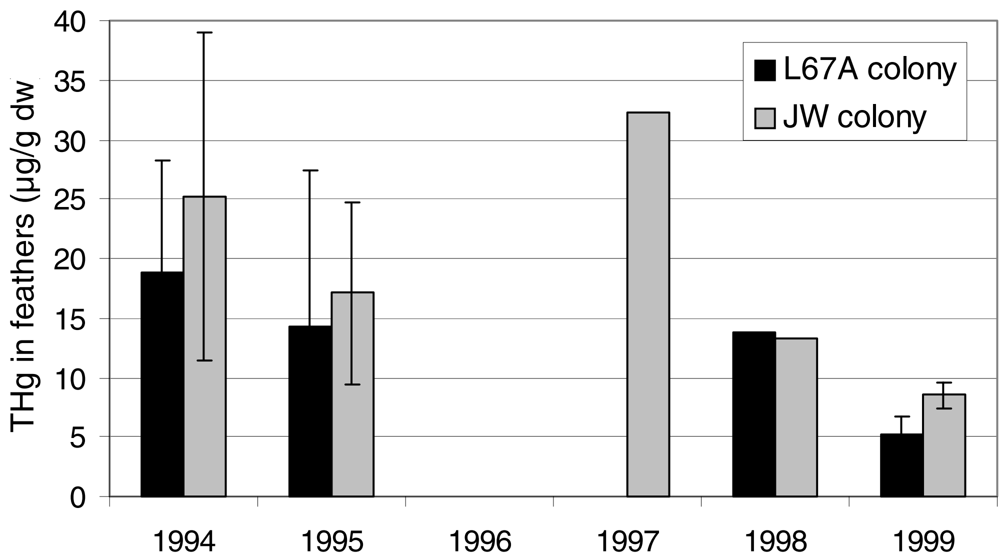


**Figure 7-5.** Total mercury residue trends in Great Egret nestling feathers in South Florida.

## Ecological Risk Status and Trends

Wading birds like the great egret could be at a potentially ecologically significant risk at the population level from the toxic effects of methylmercury present in their preferred prey (Frederick et al., 1997). However, this concern cannot be supported by the incidences of methylmercury-related toxic effects observable in highly exposed great egret colonies in WCA-3A in terms of hatching success, hatchling survival to fledging, egg laying, or egg viability. There is a potential for toxic effects in post-fledging juveniles after leaving the nest, because the most important pathway for eliminating methylmercury has been removed when feather growth ceases; however, no one has yet determined how to obtain evidence of increased mortality in this cohort away from the nest without an extensive radiotelemetry monitoring program. If there is an increased incidence of mortality in this cohort, it is not evident in the number of breeding pairs or overall reproductive success in any of the colonies under study. In fact, where total mercury concentrations in great egret feathers are highest, so is the number of breeding pairs and nests with eggs in great egret colonies (Frederick et al., 1997).

An ecological risk assessment of methylmercury toxicity to wading birds feeding in the Everglades was conducted by the District. The assessment was detailed in Appendix 7-2 and summarized in Chapter 7 of last year's Everglades Interim Report (Rumbold et al., 1999). The assessment was conducted for the wood stork, the great egret, and the great blue heron at two sites in the remnant Everglades. The first site is U3 in the interior of WCA-2A. This research site is furthest from the influence of stormwater runoff from the EAA and Lake Okeechobee releases being discharged from the L-39 canal through the S-10 structures. At U3, water column concentrations of total phosphorus are already below 10 ppb. This site already exhibits all of the physical, chemical, and biological characteristics typical of an ecosystem unimpacted by eutrophication brought about by excessive total phosphorus concentrations in the water column and peat soils.

As water column and peat soil total phosphorus concentrations decrease in agricultural stormwater runoff and Lake Okeechobee releases in response to the construction and operation of the STAs, the sites closest to the S-10 structures will eventually transition to this same unimpacted condition. Thus, the unimpacted conditions at U3 now, before the completion of the STAs (pre-STA) for the ECP, are considered representative of the conditions that will be present at even the most impacted sites in WCA-2A after the completion and operation of the STAs (post-STA). These conditions may also be referred to as pre-ECP and post-ECP conditions. The second study site is at WCA-3A-15, which is in the area referred to as the methylmercury "hot spot" in the Everglades, because fish and birds collected from this area consistently have the highest total mercury concentrations in the Everglades (USEPA, 1998; Cleckner et al., 1998; Lange et al., 1998; new data this report). If any site would present an unacceptable risk to wading birds feeding on Everglades fish, it is this site. For this reason WCA-3A-15 is considered a positive control site.

To conduct the ecological risk assessment using the hazard quotient method, the following information was obtained from the scientific literature: typical body weights and feeding rates, prey species and size preferences and methylmercury toxicity data. Actual fish total mercury concentrations were obtained from an extensive, multi-year study at both sites by FFWCC (Lange et al., 1998). A mercury concentration versus size relationship was plotted for largemouth bass and sunfish, and the mercury concentrations corresponding to the middle and maximum values of the size ranges were selected as representative of the average and maximum exposures. The average daily quantity or dose of methylmercury taken in by each bird was then calculated by multiplying together its average daily feeding rate for a typical body weight and the mercury concentration in each prey species associated with a size in the middle of its size preference range, summed over all prey species in its typical diet. The above approach was then repeated with the maximum mercury concentrations corresponding to the maximum fish size consumed.

This typical daily dose was then divided by the typical weight of the bird to obtain a dose rate on a per unit body weight basis. This result was then compared to the lowest valid no observable adverse effect level (NOAEL) for methylmercury toxic effects in the wood stork, great blue heron, and great egret. Toxicity testing has not been conducted on the wood stork and the great blue heron, and only limited toxicity testing has been conducted on great egret chicks (Frederick et al., 1997). As a result, it was necessary to obtain a surrogate toxicity value from the literature to conduct the required comparison. Following the example of the Great Lakes Initiative (USEPA, 1993), the mallard duck was selected for this purpose. The mallard duck lowest observable adverse effect level (LOAEL) of 0.064 was divided by a factor of two to approximate the NOAEL. However, there was no attempt to protect for potential inter-species differences in sensitivity to methylmercury toxicity, so the estimated mallard duck NOAEL was divided by a factor of one, as recommended by USEPA (1997), because a thorough review of the literature indicated that the mallard duck was more sensitive to methylmercury than fish-eating birds for every life stage, dose range, and toxic effect endpoint tested (Rumbold et al., 1999).

The results of last year's deterministic ecological risk assessment indicate that wading birds feeding exclusively at unimpacted WCA-2A-U3 reference site (annual average total phosphorus <10 ppb) under pre-STA conditions are at an acceptable risk of adverse effects from methylmercury exposure, even when the maximum concentrations in preferred prey are substituted for average values. This year's probabilistic risk assessment in **Appendix 7-3b** supports last year's deterministic results and conclusions in this regard. The situation is not the same in WCA-3A at the methylmercury "hot spot" at WCA-3A-15, however. There the pre-STA risks may be considered unacceptable, even for birds receiving average exposures to methylmercury in their diet. This finding is consistent with the results of laboratory dosing studies of great egret chicks (Bouton et al., 1999) and field observations of WCA-3A colonies (Frederick et al., 1997; 1999), which suggest that the WCA-3A great egret populations are at the threshold of significant toxic effects from methylmercury exposure in the diet. However, statistically significant inverse correlations between methylmercury exposure rates or body burdens and reproductive success are not evident. Continuing the exposure and effects studies of the populations of highly exposed wading birds in WCA-3A should be a priority for SFMSP Phase 2 mercury studies.

## ALLIGATOR

### Contamination Status and Trends

Adult alligators are arguably the top predator in the Everglades, and are therefore likely to be highly exposed to methylmercury through their diet. While there is now no routine monitoring of Everglades alligators for methylmercury bioaccumulation status and trends, various research projects have investigated mercury concentrations in South Florida adult alligators since 1985 (Delany et al., 1988). Mercury concentrations in muscle tissues collected in 1989 have ranged from a mean of 1.4 ug/g w. wt in adult alligators collected in Canal L-35b to a mean of 3.13 ug/g wet wt in adult alligators from WCA-3 (Hord et al., 1990; FPIC, 1991). Analyses conducted on adult alligators in 1992 and 1993 found average muscle mercury concentrations around 2.7 ug/g wet wt. in animals taken from WCA-3 and ENP (Heaton-Jones et al., 1997). Yanochko et al. (1997) reported mercury concentrations in muscle averaging around 1.2 ug/g wet wt. in adult alligators taken from WCA-3.

Mercury analysis in alligator eggs has been the subject of very few studies. Ogden et al. (1974) reported 1972 concentrations in four alligator eggs from Shark River Valley at an average of 0.69 ug/g wet wt. and an average of 0.09 ug/g wet wt in five crocodile eggs from Florida Bay. A follow-up study by Stoneburner and Kushlan (1984) reported a concentration of 0.13 ug/g wet wt. in crocodile eggs collected in 1980. In 1984, seven alligator eggs from Lake Okeechobee yielded undetectable (<0.03 ug/g) concentrations of mercury (Heinz et al., 1991).

### Ecological Risk Status and Trends

Despite what appear to be elevated mercury concentrations in the Everglades alligator, Heaton-Jones et al., (1997) reported that no signs of neurotoxicosis were observed in captive animals and histology of brain, retina, kidneys and liver showed no evidence of disease or toxicity. These findings are consistent with work on dosed captive animals. Peters (1983) dosed captive adult alligators that resulted in muscle mercury concentrations ranging between 2.3 and 2.9 ug/g wet wt. and observed no neurological symptoms of mercury toxicity. Thus, while the requisite controlled methylmercury toxicity studies have not been conducted on the adult Everglades alligator, the toxicity threshold value may be higher than its current level of exposure in the Everglades.

To date, no methylmercury toxicity studies on alligator and crocodile (crocodilian) eggs have been conducted. However, at this life stage of the developing embryo, the reptile and bird are the most similar both anatomically and physiologically. Therefore, it could be argued that, in the absence of other data, bird egg toxicity studies could be used to conduct a preliminary evaluation of mercury risks to alligator eggs. Using this line of reasoning, it would appear that the concentration reported by Ogden et al., 1974, of 0.69 ug/g wet wt. in alligator eggs approaches but does not reach the egg-Hg residue lower level of 0.75 ug/g wet wt. derived from Heinz (1979) for mallards. The concentrations in eggs collected more recently are likely to be higher, however.

Although alligator egg concentrations of methylmercury appear to fall within a range of potential concern, Heaton-Jones et al., 1997, point out that the current population estimate for the Everglades alligators is 50,000 individuals, with no indication of reproductive impairment. Further investigation of population-level impacts on alligators using uncontrolled field studies would require a multivariate analysis that accounted for the effects of other stressors, as well, including exposure to other toxic substances like DDT and PCBs, both of which have been detected in fish in the Everglades canal system (Haag and McPherson, 1997). Controlled laboratory studies of alligators may be required to address concerns for this species raised by the Science Subgroup of the South Florida Ecological Restoration Task Force (SSG, 1997).

## OTTER AND MINK

Only limited research has been conducted on the foraging preferences of the otter and mink in the Everglades, but both are believed to derive the majority of their prey from the aquatic food web (Smith, 1980; Kilham, 1984; Sample and Suter, 1999). As a consequence, both species can be considered highly exposed to methylmercury, and the limited data on methylmercury residue levels in Everglades otter indicate that it can bioaccumulate substantial concentrations (FPIC, 1991). A screening study conducted by the District revealed that the otter could be at substantial risk of methylmercury toxic effects if it includes as little as 25 percent fish in its diet (Fink and Rawlik, 1998). Despite these observations and findings, neither the otter nor the mink has been identified as requiring priority attention for protection from methylmercury risks. Nevertheless, because top-predator fish concentrations have declined over the last five years at many Everglades locations, an update to this earlier screening-level exercise appears warranted.

The Everglades otter population is believed to be reasonably abundant, and may enjoy expanded habitat associated with the District's canal system. On the other hand, the Everglades mink population is considered endangered (Humphrey, 1992), and sightings are rare (Smith and Cary, 1982; J. Ogden, SFWMD, personal communication, 1999). The otter is extant throughout the Everglades, but mink appear to have a range limited to BCNP, the Park and Miami-Dade County (Humphrey, 1992; Smith and Cary, 1982). The quantity and quality of the water flowing into the mink's range are not likely to be strongly influenced by the ECP, so mink exposures and risks are unlikely to be a sensitive indicator of post-ECP mercury-related impacts. Nevertheless, it is possible to conduct such a deterministic ecological risk assessment for the mink and the otter at well-studied sites at screening-level to determine whether follow-up studies are warranted.

Data on food habits of the mink are sparse, but based on an analysis of 16 scats collected in the Park, Smith (1980) has reported that the average mink diet consists of 64 percent crayfish, 18 percent fish, and 18 percent small mammals. Lacking data on the actual biomass of prey consumed, as a first approximation, it was assumed that the number frequency average and biomass-weighted average fractions of the diet were the same. It was also assumed that the largemouth bass is a representative top-predator fish in the mink diet. Since the size distribution and species types of the fish in the mink diet are unknown, the average largemouth bass value was used as a surrogate for the size- and diet preference-weighted average fish concentration. This is likely to bias the exposure estimates high, but this is appropriate for a screening-level exercise. Average whole fish concentrations were estimated from the data set supplied by Ted Lange (Lange et al., 1999) using an adjustment factor of 0.695 for translating fillet values into equivalent whole fish values (Lange et al., 1998). The values for the crayfish and small mammals were generated from the same data using the same approach as in **Appendix 7-4** for the Florida panther. For the purpose of this exercise, the ingestion rate of 0.15 kg/day and a toxicity reference value (TRV) of 0.016 mg/Kg-day were adopted from the Great Lakes Initiative (USEPA, 1993).

The well-studied sites WCA-2A-U3, WCA-3A-15, and L-67 were evaluated for this exercise, even though all three sites are probably too far north to fall in the range of the Everglades mink. The hazard quotients were calculated by dividing the exposure generated by the weighted-average diet by the TRV. For the typical mink diet, this resulted in hazard quotients of 1.7 at L-67, 2.2 at WCA-3A-15 and 1.4 at WCA-2A-U3. Mink feeding solely on fish from these sites would experience an even greater risk, resulting in corresponding hazard quotients of 7.1, 5.1 and 4.2. For perspective, however, it is important to compare this result to that for the Lowest Observable Adverse Effect Level (LOAEL). For the female mink, a LOAEL of 0.15 mg/Kg-day was reported in a 93-day feeding study, with a toxicological endpoint of observed nerve tissue lesions but no overt clinical symptoms (Wobeser et al., 1976 as cited in Wolfe et al., 1998). The corresponding NOAEL in this study was 0.046 mg/Kg-day for the female mink. While this is higher than the TRV used in this analysis, if the same proportion between the LOAEL to NOAEL is assumed to hold, then the equivalent LOAEL would be 3.3 times the NOAEL or 0.053 mg/Kg-day. The corresponding hazard quotient based on the LOAEL are then 0.5, 0.7 and 0.4 at L-67 WCA-3A-15 and WCA-2A-U3, respectively, for the typical diet preference scenario and 1.5, 2.1 and 1.3 for the fish-only diet preference scenario. This would appear to explain the continued survival of the endangered mink in the Everglades despite its continuing high exposures to methylmercury in its diet.

It is appropriate to use the mink NOAEL and LOAEL for the otter (USEPA, 1993). Although the work of O'Connor and Nielsen (1981) suggests that the mink is more sensitive than the otter to the toxic effects of methylmercury, conservatism in a screening-level risk assessment is appropriate, so an interspecies adjustment factor of 0.5 was chosen. The otter consumes less food per unit body weight than the mink, but its diet is composed almost exclusively of aquatic animals. Of the portion of the diet that is fish, the otter probably consumes proportionally larger fish than the mink, as well. When small mammals are eliminated from the diet mix but the same preference for crayfish as the mink is retained, the "typical" otter feeding scenario for L-67, 3A-15 and U3 results in hazard quotients of 3.5, 4.9, 2.9, while the fish-only feeding scenario produces hazard quotients of 7.7, 10.7 and 6.3. Assuming that the mink LOAEL also applies to the otter, the LOAEL hazard quotients for the typical and fish-only diets become 1, 1.5 and 0.9 and 2.3, 3.2 and 1.9, respectively. Although the otter hazard quotients are probably biased high by an inappropriately low TRV based on the mink, these results suggest that the otter should be studied in greater detail both for methylmercury exposure and toxic effects.

WCA-2A-U3 is the reference site for evaluating the likelihood of post-STA ecological risks to highly exposed fish-eating animals. This is too far north of the known range of the endangered Everglades mink but not for the otter. The likelihood is low that individual otter will experience significant toxic effects from methylmercury exposure when feeding exclusively at WCA-2A-U3 under a typical foraging scenario. Therefore, it is unlikely that individual otter will be at an unacceptable post-STA risk of methylmercury toxicity when feeding exclusively in the already impacted areas.

Methylmercury toxicity testing of the otter may not be appropriate, and, in any case, it is unlikely to be completed, peer reviewed and published before June 30, 2003. However, pharmacokinetics studies of limited intrusiveness could meet this deadline. The results of such studies would make it possible to quantify important differences between the otter and the mink in the absorption of methylmercury across the gut, the rate of transformation of methylmercury to inorganic mercury, the rates of depuration of methylmercury and inorganic mercury, and the dispositions of methylmercury and inorganic mercury in the various organs and tissues where toxic effects are manifest. This should substantially reduce the uncertainty in the application of the mink NOAEL to the otter.

Based on the above identified data gaps, the District recommends the following additional studies:

- Otter and mink feeding habits;
- Otter and mink methylmercury uptake, disposition and elimination (pharmacokinetics); and
- Routine monitoring of the otter.

This additional information will support a more accurate ecological risk assessment for the mink and otter, and provide for monitoring of status and trends of contaminant levels in the otter to gauge its on-going methylmercury exposures and risks.

## FLORIDA PANTHER

Florida panther populations in South Florida have declined precipitously through the decades of the 1970s and 1980s. This has been attributed to increased incidences of reduced litter sizes and survival rates, disease, intra-species predation, and car accidents, as the area of desirable habitat and the quality of forage have declined and the degree of inbreeding has increased (Roelke and Glass, 1992). To relieve the threat of immediate extinction due to inbreeding, the responsible federal and state agencies adopted a recovery plan that required outbreeding of the Florida panther with Texas cougars, its nearest genetic relative (M. Dunbar, USFWS, personal communication, 1996). The implementation of the plan began in 1997.

In July 1989, Florida panther #27, a four-year old female, died of unknown causes in the Park. Subsequent analysis of her organs and tissues for total mercury revealed a liver concentration of 110 ppm (FPIC, 1989). The Florida Panther Interagency Committee reached the conclusion that the proximate cause of death of Florida panther #27 was methylmercury toxicity. It had been reported that her last 12 meals consisted primarily of raccoons killed in the Shark River Slough area of the Park (FPIC, 1989). A re-evaluation of the necropsy report for Florida panther #27 provides an alternative explanation for her death: a uterine infection following a late-term miscarriage, still birth, or birth of short-lived neonates (S. Taylor, FFWCC, personal communication, 1998).

Subsequent evaluation of the feeding habits of the three distinct Florida panther populations suggested that the magnitude of mercury bioaccumulation was strongly correlated with the fraction of the diet that was made up of raccoons, which link the panthers to the aquatic food web via their opportunistic feeding behavior (Roelke et al., 1986; FPIC, 1991). The Florida panthers with the highest mercury residues had been feeding extensively in the Shark River Slough area and the female panthers feeding in that area had not reproduced in several years, while the moderately contaminated population in Fakahatchee Strand exhibited one-third the fecundity of the unimpacted population in the Bear Island State Game Area (FPIC, 1989). The most likely explanation for this set of observations is that reproductive stress occurs in populations crowded into undesirable habitat and forced to compete for low-quality forage like the raccoon instead of the preferred diet of hog and deer. This results in poor nutritional status, with a corresponding increase in the incidences of disease and reproductive failure (FPIC, 1989). However, the inverse correlation between methylmercury residues in blood or fur and the reproductive success of the three Florida panther populations suggested the possibility that high methylmercury bioaccumulation contributed to these outcomes (FPIC, 1989).

### Prey Contamination Status and Trends

The Florida panther preys preferentially on hog and deer, but will consume marsh rabbits, armadillos, raccoons, cotton rats, and even an occasional otter or juvenile alligator (Roelke et al., 1986; Maehr et al., 1990) when preferred prey densities are low or access to areas of high density is limited. Predation of raccoon, otter, and alligator links the Florida panther to the aquatic food chain. In the early 1990s, the raccoon and otter were added to the Florida panther monitoring program by the FFWCC. The usefulness of the raccoon contamination data obtained in the early 1990s for the Florida Panther Interagency Committee by the FFWCC (FPIC, 1991) has since been called into question. The raccoon collection protocol at some sites was reported to have involved trapping in the vicinity of areas where fish caught by humans were disposed of rather than in areas where panthers forage (S. Taylor, FFWCC, personal communication, 1998). Although some raccoon specimens have been collected and their blood, fur, or organs analyzed for total mercury since then, no new total mercury contamination data have been reported to date (T. Atkeson, DEP, personal communication, 1999). Such data may also suffer from the same limitation as that described for the previous data sets.

### Population Contamination Status and Trends

The Technical Subcommittee of the Florida Panther Interagency Subcommittee concluded that methylmercury contamination was a serious threat to the existence of the Florida panther (FPIC, 1989). As an intermediate remedy, the Subcommittee recommended that monitoring of panther blood continue, and that panthers with whole blood concentrations exceeding 1.7 ppm should be immediately removed from the wild, while the appropriate course of action for panthers with whole blood concentrations of 1.4-1.7 ppm wet weight would be determined by the Subcommittee on an emergency case-by-case basis. In 1998, the FFWCC announced that data collected over the last decade supported the finding that mercury contamination in previously impacted Florida panther populations had declined substantially over that period, which would be consistent with the observed trends in largemouth bass and wading birds discussed above. FFWCC is reportedly involved in a complete reevaluation of all data relevant to mercury exposure and effects in the Florida panther populations in South Florida (T. Logan, FFWCC, letter to T. Atkeson, DEP, 1998). That re-evaluation was not available at this writing. In the meantime, the FFWCC website continues to cite the results of the 1989 and 1991 reports, without caveat.

### Ecological Risk Status and Trends

Screening-level ecological risk assessments have been conducted for the Florida panther feeding on raccoon, because the raccoon links the Florida panther to the aquatic food web. From these assessments it was concluded that panthers that consume raccoon routinely are at an elevated, perhaps substantial risk of chronic toxic effects from methylmercury exposure (Jurczyk, 1993). Unless methylmercury concentrations in the raccoons of the southern Everglades have declined substantially over the last decade, Florida panthers feeding on raccoons from this area could still be at a substantial risk of chronic toxic effects from methylmercury exposure.

At present, the fractions of aquatic life in the raccoon diet and the fraction of raccoon in the Florida panther diet have not been adequately quantified. The Florida panther population in the Fakahatchee Strand State Game Area was reported to consume raccoon at the rate of 45 percent on a diet frequency basis (Roelke et al., 1986). However, subsequently this value has been challenged as unrealistically high. These data gaps and uncertainties can be addressed with estimated values that are otherwise consistent with environmental conditions. In theory, these values can be estimated by calibrating observed residue levels in the raccoon and Florida panther to values estimated from the appropriate diet. This can be done using a one-compartment model of methylmercury uptake and elimination. Residue levels in individual organs can then be calculated from the whole-body concentrations using organ-to-whole body ratios obtained from the appropriate literature. This calibration exercise was conducted for WCA-3A raccoons collected in 1990-1991, the last period for which such data are available (T. Atkeson, DEP, personal communication, 1999). Based on this calibration exercise, fish make up only about six percent of the raccoon diet, with no top-predator fish involved. Absent better information, the remaining fraction of the diet was distributed evenly between frogs and crayfish. Following the same approach for the Florida panther, the raccoon was estimated to make up about 32 percent of the diet in the Florida panther population in the Fakahatchee Strand State Game Area in 1989-1991.

To complete this exercise a domestic cat methylmercury NOAEL of 0.0134 mg/Kg (Houpt et al., 1988) was selected and multiplied by an interspecies adjustment factor of 0.5 to approximate the NOAEL of the Florida panther. The 1993 and 1997-1998 methylmercury concentrations in WCA-3A-15 fish, frogs and crayfish were used to calculate the average methylmercury concentrations in the raccoon diet. Using the previous assumptions and information, the hazard quotients of 5.8 and 4.0 were calculated for 1993 and 1997-1998, respectively.

The questions raised about the validity of the raccoon data discussed earlier (S. Taylor, FFWCC, personal communication, 1998) also apply to the ecological risk assessments based on those data. FFWCC is reportedly involved in a complete reevaluation of all data relevant to mercury exposure and effects in the Florida panther populations in South Florida (T. Logan, FFWCC, letter to T. Atkeson, DEP, 1998). The results of that reevaluation were not available at this writing. However, the results of the above modeling exercise suggest that the raccoons collected for total mercury analysis in 1990-1991 in South Florida by the then Florida Game and Fresh Water Fish Commission did not contain inappropriately high methylmercury concentrations in their bodies. Thus, it is unlikely that these raccoons were feeding atypically on fish remains discarded near fish camps and garbage disposal areas rather than on a more typical mix of aquatic life at a more typical rate.

## HUMANS

### Population Contamination Status and Risks

A study conducted by the Centers for Disease Control at the request of USEPA Region 4 found no substantially elevated concentrations of total mercury in the hair of human volunteers known to consume fish caught in the Everglades canals and marshes, including members of the Miccouskee Tribe of Indians (CDC, 1994; Fleming, 1995). However, it is not clear that this study adequately captured the mercury contamination levels in highly exposed subsistence fisher populations like members of the Miccosukee Tribe of Indians engaging in a traditional lifestyle. There are no new data on mercury contamination levels from studies of volunteers from the Everglades fishing community.

There are no reported incidents of methlymercury toxicity in humans consuming large quantities of alligator, fish, or raccoon flesh, but there have been no new systematic studies to take reports of or independently measure such effects.

## ADEQUACY OF CLASS III WATER QUALITY STANDARD

The District documented no violations of the total mercury Class III Water Quality Standard of 12 ng/L in any canal (unpublished data, **Appendix 7-2**) during the 1998-1999 water year. However, dredging upstream of the S-5A Pump Station in the C-51 canal resulted in a near exceedance in June of 1999. Yet during this same period the fisheries remained impaired due to the exceedance of the Florida no consumption or limited consumption action levels (Lange et al., 1999). This again underscores the need to revise the Class III Water Quality Standard downward to reflect largemouth bass bioaccumulation factors as high as 10,000,000. If the Florida limited consumption action level of 0.5 ppm is divided by 10,000,000, the corresponding methylmercury concentration in water is 0.05 ng/L. If methylmercury is as much as one-third of total mercury in a worst case, the corresponding total mercury water quality standard would be 0.15 ng/L, or almost two orders of magnitude lower than the present 12 ng/L value.

The question then arises as to whether a methylmercury action level of 0.5 mg/Kg in largemouth bass to protect human health would be fully protective of the wood stork, the otter, the alligator, and the Florida panther. This analysis is conducted for the Florida panther in **Appendix 7-4**.

Using the previous assumptions and information, the aquatic food chain methylmercury concentrations at WCA-3A-15 were adjusted proportionally downward to be equivalent to a largemouth bass flesh concentration of 0.5 mg/Kg. The hazard quotient was calculated to be 2.2. When WCA-3A-15 fish consumption by the raccoon was eliminated altogether, the hazard quotient for a Florida panther preying on such raccoon was still about 1.9. This indicates the importance of frogs and crayfish in the Florida panther food chain. Only when the raccoon was eliminated from the diet altogether did the hazard coefficient for methylmercury toxicity to the Florida panther approach 1.

Some have suggested that adopting a revised Water Quality Standard for total mercury equivalent to the sport-fish action level will also be fully protective of wildlife, including the endangered Florida panther. To the contrary, Florida panthers routinely feeding on Everglades raccoons may not be fully protected by a Water Quality Standard derived from the present-day sport fish action level to protect human health. For panthers that consume juvenile alligator and otter more than occasionally, the methylmercury exposures and risks would increase disproportionally, because both the alligator and otter consume large fish.

However, there are substantial uncertainties in this analysis. To reduce these uncertainties, follow-up studies of methylmercury pharmacokinetics and toxicology for the Florida panther are recommended. The recommended studies are summarized in the section that answers the question: What is the status of District and DEP efforts to understand and solve the Everglades mercury problem?

# CAN THE CONTROL OF LOCAL SOURCES REDUCE EVERGLADES MERCURY RISKS?

## SUMMARY

STAs that perform like the ENR Project will reduce inflow total mercury by between 50 percent and 75 percent prior to discharge to the already impacted areas of the northern Everglades. This may have some positive effect on methylmercury production and bioaccumulation in fish in these areas, because both methylmercury production and fish tissue concentrations have been determined to be proportional to the total mercury concentration in the underlying hydrated peat soil. However, for the Everglades as a whole, atmospheric deposition contributes more than 95 percent of the new mercury inputs each year, and only a reduction in atmospheric deposition will reduce the average concentration of total mercury in peat soils over the nearly 10,000 square kilometers (4,000 square miles) of the Everglades.

There is still great uncertainty as to the relative contributions of local sources and global background to the annual atmospheric deposition of mercury to the Everglades. A study is planned for the beginning of 2000 that should determine whether the air above the influence of local air emissions sources in what is called the free troposphere could itself be a source of enough gas-phase inorganic mercury to supply the observed high rates of inorganic mercury in rainfall during South Florida's wet season. New air emissions source, transport, and deposition monitoring and modeling in South Florida in water year 1999-2000 should help resolve the contribution of local sources to the wet and dry deposition total. The reported declines in total mercury concentrations in fish and birds at several locations in the Everglades over the last decade may be attributed to the reported 65 percent decrease in mercury emissions from municipal incinerators in South Florida during the same period. However, a decrease in the U.S. background may have also begun several decades ago, so it cannot yet be determined whether the Everglades is responding to local source reduction, U.S. background declines, or to some other factor, like higher average flows and water depths or the absence of fires during this same period. However, a decrease in the U.S. background levels may have also begun several decades ago, so it cannot yet be determined whether the Everglades is responding to local source reduction, U.S. background declines, or to some other factor, like higher average flows and water depths or the absence of fires during this same period.

To address the question of mercury risk reduction through source control, several related questions arise, including:

- What is the mercury load contribution of stormwater runoff transport to the Everglades?
- What is the mercury load contribution of atmospheric deposition transport to the Everglades?
- What fraction of the atmospheric deposition load is from local sources versus global background?
- What is the mercury load contribution groundwater transport to the Everglades?
- What is the mercury load contribution of recycled mercury from the contaminated peat soil to the Everglades?

These questions are answered below.

## LOCAL STORMWATER RUNOFF SOURCES

### Lake Okeechobee Releases and EAA Stormwater Runoff

The concentration data collected by the District's in its upper canal system continue to support the conclusion that the Lake Okeechobee releases and EAA runoff do not constitute a significant source of either total mercury or methylmercury to the northern Everglades as a whole. As calculated elsewhere (USEPA, 1998) and reported in last year's Everglades Interim Report (Fink et al., 1999), stormwater runoff contributes less than five percent of the new total mercury entering the vast majority of Everglades each year. However, this is unlikely to be the case for the STAs and for the areas closest to the points of discharge to the northern Everglades, since the quality and quantity of the water flowing through both are dominated by EAA runoff. In the ENR Project, about 50 percent and 75 percent of the annual supply of total mercury and methylmercury, respectively, originated with the inflow pump. The higher hydraulic loading rates of water through STAs 1, 2, 3/4, and 5 should result in even higher percentages of removal than for the ENR Project.

The downstream influence of Lake Okeechobee releases and EAA runoff on inorganic mercury deposition near the District's structures has been inferred from the mercury analysis of radiodated sediment cores collected at F1, about 1.8 km downflow of the S-10C structure, and the most runoff-impacted site routinely studied in WCA-2A. These results showed a much higher total mercury deposition rate over the last 50 years than cores collected farther downstream, suggesting to the principal investigators that EAA runoff load was being deposited there at a disproportional rate (J. Keeler, University of Michigan, personal communication, 1999). The influence of Lake Okeechobee releases and EAA runoff on the already impacted area in WCA-2A downstream of the S-10 structures is the subject of a modeling task required under a DEP contract with TetraTech, Inc. The results will be reported in next year's chapter on the Everglades Mercury Problem.

### STAs

As demonstrated in **Appendix 7-5**, the STAs that function like the ENR Project are likely to reduce the total mercury load in EAA runoff in the range of 50 percent to 75 percent, which should have some, perhaps significant benefit to the already impacted areas of the northern Everglades. If this is the case, then, all other things being equal, a reduction in the EAA runoff load via filtering through the STA 1W should reduce the rate of deposition of total mercury in the already impacted areas nearest the point of discharge, which, in turn, will reduce the concentrations of inorganic mercury in the hydrated peat soil.

There is a correlation between the total mercury concentration in hydrated peat soil and methylmercury production (C. Gilmour, ANS, personal communication, 1999) and bioaccumulation in fish (D. Krabbenhoft, USGS-Madison, personal communication, 1999). This suggests that a reduction in the total mercury concentration in the surface sediment at F1 will result in a corresponding reduction of the methylmercury concentrations in fish at F1. This positive effect will be offset somewhat by the likely reduction in the rate of peat production associated with a reduction in water column phosphorus concentrations, but it is unlikely to be offset completely. The benefits of this load reduction have been modeled using the Everglades Mercury Cycling Model-1. The results of this modeling application were detailed in Appendix 7-4 of last year's Everglades Interim Report and are summarized in the subsection that answers the question, What tools are needed to understand and solve the Everglades mercury problem? This modeling exercise will be repeated with the Everglades Mercury Cycling Model-2 by TetraTech under contract to DEP. The result of this modeling effort will be reported in next year's chapter on the Everglades Mercury Problem.

## ATMOSPHERIC DEPOSITION

### Local Air Sources

The debate continues regarding the benefit to the Everglades from reducing local sources of mercury air pollution. Using elemental tracers for source apportionment, one estimate of local air source contributions to the Everglades arrived at value of 71 ±8 percent for oil and municipal waste combustion sources, with the remainder accounted for by medical waste incineration through emissions reconciliation (Dvonch et al., 1999). A separate modeling exercise supported the results of the source apportionment analysis (Marsik et al., 1999). Taken together, these lines of evidence suggest that the supply of mercury from local air emissions sources to the Everglades is as high as 95 percent (J. Keeler, University of Michigan, personal communication, 1999). These analyses ignored the contribution of the annual burning of the sugar cane fields, but it is calculated to be low (Patrick et al., 1994). Based on elemental tracer analysis and source modeling using FAMS data (Guentzel et al., 1997), others have arrived at estimates of local source contributions to South Florida as low as 30 percent (W. Landing, FSU, personal communication, 1997). To make up the difference, the global reservoir must contribute 70 percent. A description of the mechanism by which this could occur is taken up in the next section.

As noted in the previous section, there appear to be downward trends in the concentrations of methylmercury in largemouth bass and great egret feathers and eggs at some well-studied sites in the Everglades. It is possible that these downward trends are indicative of the beneficial effect of local source reduction brought about by the passage of rules by the Environmental Regulation Commission (ERC) in 1993 that provide for voluntary and then mandatory reduction of mercury in feedstocks to municipal incinerators. Using mercury emissions reports from permitted facilities, DEP has calculated as much as a 65 percent reduction from the annual mercury emissions rate in South Florida at the beginning of the decade (T. Atkeson, DEP, personal communication, 1999). The mercury concentrations in municipal waste combustor emissions from South Florida are depicted in **Figure 7-6.**

If this is the cause of the apparent downward trends in fish and birds, this would be desirable for two reasons. First, it means that local sources, which can be controlled, are making a substantial contribution to the Everglades atmospheric deposition load, rather than the atmospheric deposition load being dominated by global background. The

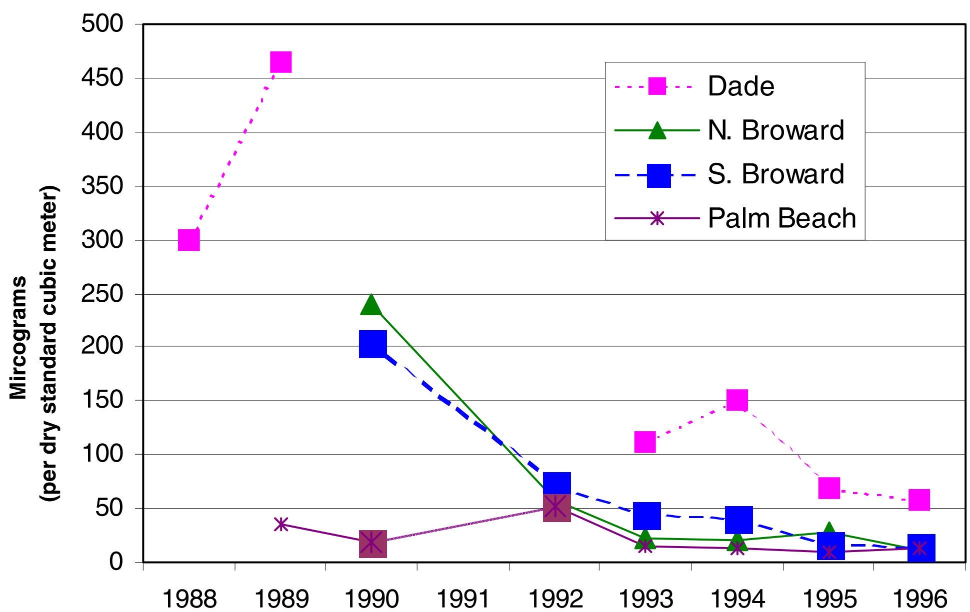


**Figure 7-6.** Mercury concentrations in South Florida municipal waste combustor emissions over time (Source: T. Atkeson, DEP).

control of global background is outside the authority of either DEP or USEPA, and only an international treaty could bring about the required reductions in worldwide emissions. Second, the rapid response of the Everglades to local source reduction may be attributed to the observation that the overlying water column is usually in excess of inorganic mercury relative to underlying peat pore water as a result of rainfall (D. Krabbenhoft, USGS-Madison, personal communication, 1999), and that this excess inorganic mercury is taken up by the surficial peat soil for subsequent methylation (G. Gill, TAMUG, as cited in Gilmour et al., 1998b), rather than the methylation process being fed primarily by the release of inorganic mercury from the peat soil reservoir below. This would mean that the response time of the Everglades is not on the order of decades, as predicted by the USEPA Everglades Mercury Cycling Model-1, but on the order of years.

However, this speculation must be reconciled with the observation that the inorganic mercury deposition rates over North America at some locations appear to be declining over the last 20 to 40 years (Benoit et al., 1994). This is also consistent with the reports that mercury deposition appears to have peaked in Florida Bay in the mid- to late-1950s (T. Atkeson, DEP, personal communication, 1997). This is probably in response to early efforts to shift from open burning of refuse to landfilling and subsequent voluntary reductions in the use of mercury in certain industrial processes (e.g., chlor-alkali production) that preceded voluntary substitution of other materials for mercury in various household and commercial products. If the Everglades is responding to a 20- to 40-year decline in background mercury concentrations over North America rather than a 10-year decline in local air emissions sources, then its response time to atmospheric load reduction is probably more on the order of decades than years. This is still not bad news, but it confounds the inference that local source reduction is linked to the recent 5-year decline in mercury concentrations in Everglades fish.

### Global Background

There is a body of evidence that suggests that the global reservoir is making some, perhaps a substantial contribution to the atmospheric deposition of mercury to the Everglades. For most pollutants in most locales, the concentration of the pollutant decreases over time with the intensity and duration of rainfall, indicating that the reservoir in the lower atmosphere is being depleted over time. According to the results of special studies conducted under the Florida Atmospheric Mercury Study (FAMS), this is not always the case in South Florida (Guentzel et al., 1997). In South Florida, summer rainfall concentrations always exceed those of the dry season, but they do not decrease substantially with the duration of rainfall, suggesting that there is a large pool of reactive gaseous mercury that is being scavenged without substantial depletion.

Dry and wet season air campaigns are planned for January and July 2000 to collect air samples in the free troposphere for near real-time analysis of elemental mercury and reactive gaseous mercury. The presence of high concentrations of reactive gaseous mercury in the free troposphere will establish only that the global reservoir could make a substantial contribution to rainfall deposition on South Florida during the wet season, not that it is making such a contribution. On the other hand, its presence in only trace concentrations in the July 2000 campaign will establish that such a contribution is not possible. A more detailed discussion of the planned studies is taken up in the section that answers the question: What is the status of District and DEP efforts to understand and solve the Everglades mercury problem?

### Rainfall

The District participates in the Mercury Deposition Network (MDN) of the National Atmospheric Deposition Program to meet its rainfall compliance monitoring requirements under its federal and state permits to operate the STAs. Bulk rainfall was collected weekly atop 48-ft towers at the ENR Project, the Andytown Substation at U.S.

27 and I-75, and the Park Research Center. While there was high week-to-week variability in total mercury concentrations within and between sampling sites, the same deposition rate patterns were observed on a monthly and annual average basis as in the Florida Atmospheric Mercury Study or FAMS (Guentzel et al., 1997) that ended its collections at these same sites in December 1996. **Figure 7-7** displays the monthly rainfall data collected under the preceding FAMS and the volume-weighted monthly average calculated from the weekly MDN data generated from the present weekly permit compliance monitoring program. There was a break in the monitoring program between January 1997, following the end of FAMS, and January 1998, when the Andytown site came back on line under the MDN. Although not statistically significant, over the last five years there appears to be a slight decline in the average concentrations at all three sites during the dry season, but no difference can be discerned during the wet season.

## GROUNDWATER BACKGROUND

A joint screening study conducted by the USGS and the District indicates that Everglades groundwater is not generally highly contaminated with either total mercury or methylmercury (Harvey et al., 1999). In most instances, the total mercury concentration is not statistically significantly different from the overlying surface water, and methylmercury concentrations are often undetectable at 10- and 40-foot depths (unpublished District data; Harvey et al., 1999). The general direction groundwater flux is down, and in locations where upward flux occurs in the vicinity of WCA-1, the rate decreases rapidly with distance from the L-7 and L-39 levees surrounding WCA-1, which is held at a higher stage than the surrounding farmland and WCA-2A (Harvey et al., 1999). Taken together, these facts suggest that groundwater cannot make a significant contribution to the total mercury or methylmercury inputs to the Everglades, but where localized discharge areas occur, enhanced transport of inorganic mercury or methylmercury from the underlying peat soil pore water may occur (King, 1999).

For example, it has been observed that total mercury concentrations are higher at WCA-2A-F1, which is 1.8 km form the L-39 levee, than WCA-2A-U3, which is 10.8 km away, on infrequent occasions during extended periods of no rainfall

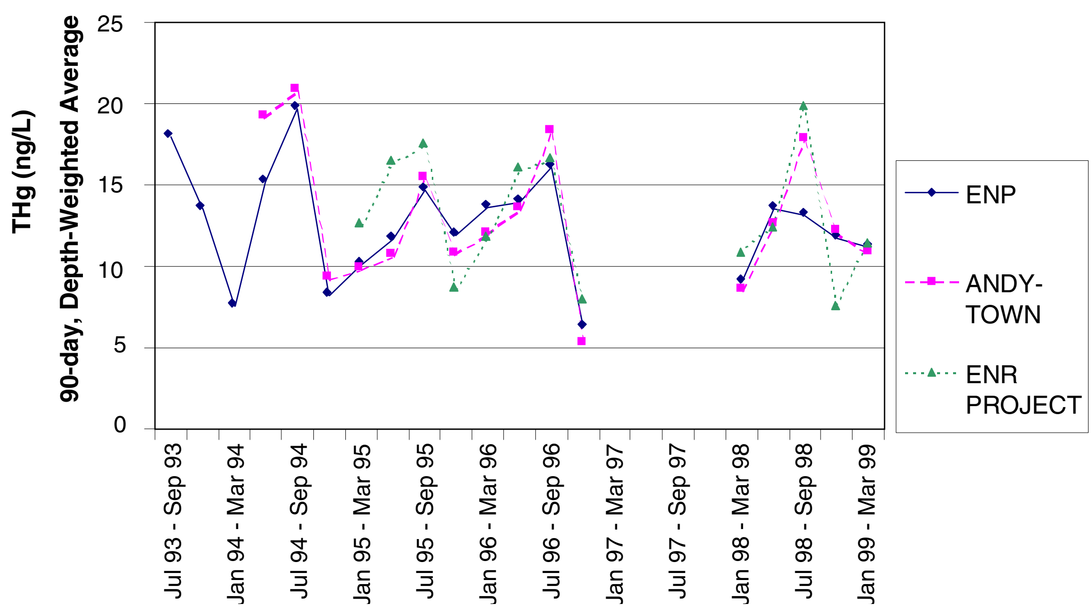


**Figure 7-7.** Total mercury concentrations in monthly average bulk rainfall over time.

and no flow through the S-10 structures into WCA-2A. This suggests that the upward flux of about 0.1 cm/day (Harvey et al., 1999) can make a small but observable contribution to the concentrations of total mercury in the overlying water column. Any such effect on methylmercury concentrations in the water column is probably being dwarfed by the generally higher rates of methylmercury production at WCA-2A-U3 than WCA-2A-F1, but these differences may be smallest in the winter when microbial activity slows under the influence of lower water column temperatures and it is during the winter when the extended periods of no rainfall and no flow are most prevalent.

## RECYCLED PEAT SOIL MERCURY

As noted in the above discussion of local source contributions, USGS scientists have observed that, on average, the concentration of inorganic mercury in the overlying water column appears to exceed the corresponding concentration in the pore water of the underlying surficial peat soil (D. Krabbenhoft, USGS, personal communication, 1999). This excess is believed to be driven by wet and dry atmospheric deposition. This results in a net transfer of inorganic mercury from the water to the peat soil on average. This net transfer has also been observed by Gary Gill and co-workers using flux chambers to measure the magnitude and direction of inorganic mercury and methylmercury flux (Gilmour et al., 1998b). It is in the first two to four centimeters of peat soil that the methylation of inorganic mercury is occurring (Gilmour et al., 1998b).

The other potential source of inorganic mercury to the methylation process is the inorganic mercury that has accumulated in the peat soil that has accreted over the years. The concentration of inorganic mercury in historically deposited peat soil averages about 150-160 ug/Kg (Delfino et al., 1993), which would appear to be a substantial reservoir, but Everglades peat soil generally has a low bulk density, averaging about 0.035-08 gm/cm$^3$ in the first two to ten centimeters (Reddy et al., 1991; Delfino et al., 1993; King, 1999). While this should facilitate diffusive exchange, it diminishes the actual mass per unit volume of inorganic mercury stored on soil solids. Nevertheless, if all of the inorganic mercury sorbed to or incorporated in the soil solids were available, assuming a mean bulk density of 0.045 g/cm$^3$, it would be the equivalent of about 7 ug/L, more than three orders of magnitude greater than the concentration of inorganic mercury in the overlying water. However, if the potentially bioavailable fraction is the truly dissolved fraction, then the concentration of potentially bioavailable inorganic mercury in peat soil is actually quite low. Gary Gill and co-workers at Texas A&M University-Galveston have performed sediment chamber studies to measure the flux of total mercury and methylmercury into and out of the sediment. In a limited scoping study conducted at WCA-2A-U3 and WCA-3A-15 in July of 1998, they found that there was a net flux of inorganic mercury into the sediments under both daylight and night conditions, while the opposite tended to be true for methylmercury, although the nighttime flux generally exceeded the daytime flux (Gilmour et al., 1998b). This suggests that the concentration of inorganic mercury in the water column is supersaturated relative to the sediment pore water, resulting in a continuous net flux into the sediment.

This observed disequilibrium between the concentration of inorganic mercury in sediment pore water and the overlying water column could be maintained by the activity of sulfate-reducing bacteria that produce methylmercury from inorganic mercury, which is then transported back out of the sediment at a rate that exceeds that predicted by a Fickian diffusion model by as much as a factor of 10 or 20 (D. Krabbenhoft, USGS, personal communication, 1999). This enhanced transport may be a consequence of dispersive processes, or it could occur in association with benthic zooplankton or other diurnally active invertebrate species that carry the methylmercury absorbed while in contact with the sediment during the day as they float into the water column at night (D. Krabbenhoft, USGS, personal communication, 1999). This might also explain the apparent increase in the nighttime over daytime methylmercury flux, which might otherwise be attributed to an increase in the nighttime over daytime production rate or a sudden change in the sorption coefficients brought about by a change in the redox potential profile of the surficial sediment. Another potentially important transport mechanism for mercury species from the sediment to the water column is dispersion and advection facilitated by methane gas ebullition from the near-surface sediments. If the sediments do become more anoxic at night, and methane gas production increases in response, then enhanced transport of mercury species to the water column at night could also be accounted for by this mechanism.

To resolve the question of inorganic mercury bioavailability and of enhanced nighttime production or transport of methylmercury, several lines of study will be pursued. They are summarized in the section that answers the question: What is the status of District and DEP efforts to understand and solve the Everglades mercury problem?

# CAN MANAGEMENT OF WATER QUANTITY OR QUALITY REDUCE EVERGLADES MERCURY RISKS?

## SUMMARY

Many factors influence methylmercury bioaccumulation in fish, including the concentration of methylmercury in living, dying and dead plant biomass, the food web structure, fish feeding preferences and prey availability, and fish growth rates and ranges. All of these factors are under the direct or indirect influence of water flow and depth or water quality. These inter-relationships were discussed in great detail in last year's Everglades Interim Report. If the Everglades responds to changes in water flow and depth like the ENR Project, then in high flow, high water years, methylmercury concentrations in water and fish should be lower than in low flow, low water years. However, the routing, timing, magnitude and duration of water flow are to be optimized for the restoration and protection of Everglades habitat. There is likely to be little flexibility in the optimum water management regimen for the regulation of methylmercury production, bioaccumulation or exposure.

Many water quality factors are known to influence methylmercury production and bioaccumulation, some of which are removed by constructed wetlands (e.g., phosphorus and inorganic mercury) and some that are not (e.g., calcium and magnesium, dissolved organic carbon, chloride, sulfate, iron). Only conventional chemical treatment systems are likely to remove these soluble, relatively biologically inert chemical constituents. However, changes in the concentrations of some chemical constituents in the northern and central Everglades might be brought about by changes in upstream farming practices. A mathematical model that captures the influences of both water quantity and quality on methylmercury production and bioaccumulation will be required to provide a rigorous, quantitative answer to the question of whether changes in the farm use of sulfur or sulfates, for example, will have a beneficial or detrimental effect. Such a model is undergoing further development and discussed in the subsection that answers the question, What tools are required for understanding and solving the Everglades mercury problem?

## MANIPULATING WATER COLUMN PHOSPHORUS CONCENTRATIONS

Where phosphorus is the limiting nutrient, an increase in water column total phosphorus is generally associated with an increase in plant densities and production rates, unless some other factor becomes limiting. As the concentration increases further, eventually the species of one-celled plants called algae that are adapted to a low phosphorus environment are outcompeted by algae species that require more phosphorus to thrive. As the water column phosphorus concentrations increase further, the excess plant production is accompanied by a more rapid decomposition of the accumulating dead plant material by bacteria that require oxygen to support their life processes. This results in an increased rate of dissolved oxygen (DO) consumption, resulting in a lowering of the average DO during the day and increasing the magnitude, depth and duration of anoxia at night when photosynthetic production of oxygen ceases and plants consume oxygen to survive. Under such conditions organisms that can tolerate low DO conditions replace those that cannot. The excess plant production, DO deficit and species shifts are the classic signs of eutrophication (Carlson, 1980; Brezonik, 1984).

Most methylmercury production and decomposition is a by-product of microbial metabolism. Sulfate reducing bacteria (SRB) are most likely to be involved in both processes in the Everglades, as elsewhere (Compeau and Bartha, 1985; Gilmour et al., 1998b; Marvin-DiPasquale and Oremland, 1998). Sulfate reducing bacteria require conditions devoid of oxygen in which to survive and thrive. Generally these conditions are found a few cm beneath the surface of the peat soil layer (Gilmour et al., 1998b). In general, the lower the water column DO concentration, the higher the density and activity of the SRB in the underlying sediment or soil. Gilmour and Henry, 1991, and Henry et al., 1995 report an increase in methylmercury production by as much as 40 times in sediments under anoxic (oxygen-free) and sulfidic (hydrogen sulfide-rich) waters than oxic (oxygen-rich, sulfide-poor) waters.

The DO profile in the surficial peat soil is determined by the DO concentration in the overlying water column, the sediment oxygen demand, and the rate of exchange of DO across the soil/water interface. With an adequate supply of organic carbon, the presence of excess phosphorus in the soil is associated with enhanced microbial activity and a higher sediment oxygen demand, so the DO profile should actually decline even more steeply than if it were being determined solely by the DO concentration in the overlying water. Taking all of these factors and conditions into account, lowering the average water column DO should then produce a more rapid decline in the DO profile in the surface sediment. In theory, this would allow the SRB to move closer to the soil surface while retaining optimum density and activity. Moving the net production of methylmercury closer to the soil surface might then increase the rate at which methylmercury is transferred to the overlying water column, depending on whether the production rate or the exchange rate is rate-limiting. This movement of the zone of maximum net methylation toward the surface of the soil might also increase the responsiveness of the SRB to short-term changes to the inorganic mercury loading rate from wet and dry atmospheric deposition. Conversely, the deeper the zone of maximum net methylation is driven by an increase in the water column DO concentration, a reduction in sediment oxygen demand, or an increase in the rate of DO exchange, the less responsive the SRB will be to short-term changes in atmospheric deposition rates and the more responsive the SRB will be to long-term changes in the average inorganic mercury concentration in the soil profile and its bioavailability.

An inverse relationship has been observed between water column phosphorus and methylmercury bioaccumulation in fish in some lakes (D'Itri, 1971; Hakanson, 1980). This phenomenon has been referred to as biodilution. The phenomenon of biodilution is brought about by the more rapid removal from the water column of inorganic mercury and methylmercury sorbed to the more rapidly growing, dying and decaying plant biomass. The remaining inorganic mercury and methylmercury is then diluted in the more rapidly growing plant biomass. The lower concentrations in water and plants are then passed up the food chain to top-predator fish. In lakes where food availability limits the rate of fish growth, the methylmercury bioaccumulating in fish may be further diluted by the more rapid addition of fish biomass. The concept and features of biodilution are taken up in greater detail in the section that answers the question: How will Everglades restoration affect mercury risks? Some have argued that the Everglades phosphorus reduction program must take such an inverse relationship with phosphorus into account to ensure that harm of one kind is not done in pursuit of reducing or eliminating a harm of another kind. Others have carried the argument further and suggested that adding phosphorus to the Everglades will solve the mercury problem. However, as noted above, through its relationship to the oxygen cycle, phosphorus may stimulate methylation as it dilutes methylmercury bioaccumulation. The net effect of eutrophication on methylmercury bioaccumulation can only be determined by experiment or a reliable predictive mathematical model.

To evaluate the efficacy of intentional eutrophication as a tool for managing methylmercury bioaccumulation, Rudd and Turner (1983) dosed mesocosms in impoundments of the English-Wabagoon River system with phosphorus and radioactive 203-Hg(II). The dosing rate used resulted in an initial water column concentration of about 15 ng/L before equilibration with the sediment in the mesocosms. This concentration range should have avoided any artifacts that could be introduced when working with inappropriately high water column concentration ranges, as was often necessary without the use of radiolabelled inorganic mercury. The authors concluded that, all other factors being equal and not limiting, an increase in algal nutrients was more likely to increase microbial mercury methylation rates and result in stable or increased mercury concentrations in fish, while lowering primary productivity would reduce methylmercury production and bioaccumulation at the expense of fish growth rates.

Quoting directly from Rudd and Turner (1983): "The overall effects of increasing primary productivity on Hg concentration of fish appear to be a complex interrelationship between stimulation of the growth rates of fish and microbial Hg methylation rate and, in some cases a change in pH, which may reduce either bioaccumulation efficiency of CH3Hg+ by fish or change the form of methylated mercury produced by microorganisms. Increases in primary productivity that were not large enough to affect ecosystem pH produced the largest increases in Hg concentration of pearl dace and crayfish. These conditions appear optimal for Hg methylation."

Laboratory microcosm and field mesocosm dosing studies with phosphorus will be conducted in the Everglades by ACME scientists over the next few years to evaluate its response to a reduction in water column total phosphorus.

## MANIPULATING WATER COLUMN SULFATE CONCENTRATIONS

In addition to a source of carbon and conditions of anoxia, SRB require sulfate to survive and thrive. The product of sulfate reduction by these microbes is sulfide. Sulfide is then oxidized back to sulfate by a different bacteria species. At very low sulfate concentrations, the density and activity of SRB are determined by the availability of sulfate. At higher sulfate concentrations, another factor may become limiting. At very high sulfate concentrations, sulfide can accumulate to high levels in peat pore water. Some scientists have hypothesized that at low sulfate and high sulfide concentrations, methylation of inorganic mercury is limited by sulfate and sulfide respectively, but there is a ratio of sulfide to sulfate that is just right for maximum inorganic mercury methylation. Where that optimum relationship occurs is probably dictated by several other factors. Wherever this maximum actually lies, the concentration of sulfate in peat pore water strongly influences the production of methylmercury. Whether it is possible or appropriate to control the concentration of sulfate in peat pore water by controlling the upstream sulfate supply then becomes a pressing management question.

Sulfur is intentionally amended to EAA soils intended for vegetable crops and sugar cane. About

500 lb per acre per year of sulfur would be applied if the sugar cane farmer followed IFAS recommendations (Sanchez, 1990), but an average annual application rate of about 33 lb per acre per year has been calculated from local purchasing records (F. T. Schueneman, IFAS, personal communication, 1999). A crude mass budget for the EAA suggests that the annual rate of loss of sulfur from the EAA is equivalent to between 30 and 40 lbs per acre. This suggests that the farmers are adding just enough sulfur per year to maintain the present sulfur concentrations in the EAA soil for optimum crop management. Much of the excess sulfate in EAA soils that is released during peat soil oxidation is probably leaching back into the underlying soil rather than being transported off-site. Otherwise, the concentrations in the District's primary canals would be much higher.

EAA runoff contributes excess sulfur to the northern and central Everglades (Bates et al., 1998). The STAs are not expected to have any substantial effect on sulfate in EAA runoff. The sulfur cycle influences the mercury cycle. However, it is premature to consider the manipulation of sulfur levels in soil or water in the already impacted area as a credible, defensible and prudent option for managing methylmercury production or bioaccumulation. More research into the relationships between the sulfur and mercury cycle is required before such options can be properly formulated and evaluated.

Laboratory microcosm and field mesocosm dosing studies with sulfate will be conducted in the Everglades by ACME scientists over the next few years to evaluate its response to a reduction in soil pore water sulfate.

## MANIPULATING OTHER WATER CONSTITUENT CONCENTRATIONS

The ENR Project did not have any statistically significant effect on calcium, chloride, sulfate, DOC, or iron concentrations in stormwater runoff. The STAs with similar underlying peat soils are unlikely to behave substantially differently. Therefore, the option of manipulating the water quality with respect to these constituents via STAs is unlikely to be effective. The effects of advanced treatment technologies on these constituents may deserve investigation. However, as several of the constituents of interest are related to peat soil farming practices, e.g., iron, sulfate, DOC, calcium and magnesium (Sanchez, 1990), in theory it might be possible to reduce or eliminate the application of these constituents by changing or eliminating certain crops. In practice, it is highly unlikely that such an option will be chosen because of its socioeconomic ramifications.

# HOW WILL EVERGLADES RESTORATION AFFECT MERCURY RISKS?

## SUMMARY

The Everglades restoration program will eventually restore a more natural water quantity and quality to the Everglades while providing for human uses of the resource in the context of a sustainable South Florida. Both water quantity and quality affect methylmercury production, bioaccumulation and exposure, so changes to either could increase or decrease the magnitude or extent of methylmercury risks in areas strongly influenced by the routing, timing, magnitude and duration of farm and urban runoff and Lake Okeechobee releases. The District has evaluated the influence of water quantity and quality on inorganic mercury transport and bioavailability for methylation and methylmercury production, decomposition and bioaccumulation using field, laboratory and modeling studies conducted under the SFMSP. The results of these three independent but interrelated approaches support the following conclusions:

- Increasing the inflow rate and water depth in the STAs during high rainfall years will decrease the interior water column concentrations and increase the removal efficiencies of both inorganic mercury and methylmecrury.
- Increase in the flow to WCA-3A will likely reduce methylmercury bioaccumulation in the "hot spot" through flow dilution.
- Decrease in phosphorus-mediated eutrophication in the already impacted areas of WCA-2A from the implementation of on-farm BMPs and of the ECP will result in some but not an ecologically significant decrease in biodilution.
- Even if the manipulation of water quantity or quality could reduce methylmercury production, bioaccumulation or exposure in theory, absent a compelling demonstration of an imminent methylmercury threat to wildlife under the present water quantity and quality regime, the habitat needs of Everglades plant and animal life will take precedence.
- Imminent methylmercury threat to Everglades wildlife cannot be demonstrated.
- Reduction in mercury air pollution over the Everglades through local air source control is the preferred approach for reducing methylmercury production and bioaccumulation in the Everglades.
- Reduction in inorganic mercury deposition to the Everglades stemming from local air pollution source control could offset the increase in methylmercury bioaccumulation associated with a decrease in biodilution in the already impacted areas.

## INTRODUCTION

There are several elements to the Everglades Restoration Program that could positively or negatively affect methylmercury production, bioaccumulation or exposure. These elements occur in successive phases. The first element requires the implementation of BMPs to reduce the total phosphorus loads to the northern Everglades by a minimum of 25 percent. This element is discussed in **Chapter 5**. Next, STAs are to be constructed to further reduce the total phosphorus in storm runoff from the EAA to 50 ppb at the point of discharge. This is considered Phase 1 of the ECP. The ENR Project was the prototype STA. Its performance in removing phosphorus and other water constituents is discussed in **Chapter 6**. In Phase 2 of the ECP, the Alternative Treatment Technologies are intended to further reduce the total phosphorus concentrations to a design target 10 ppb. This element is discussed in **Chapter 8**. Subsequently, the Restudy contemplates changes to the configuration of the canals and structures of the Central and Southern Florida water management system, including the construction of additional above and below ground surface water storage reservoirs that will provide for the sustainable water supply needs of the Everglades and the growing human population of South Florida. Each of these changes may influence inorganic mercury transport, transformation or storage and net methylmercury production or bioaccumulation. The net effect of these influences may be increased or decreased methylmercury risks to fish-eating animals and their predators.

## EVERGLADES NUTRIENT REMOVAL PROJECT

The ENR Project, the prototype STA, was a 1535-hectare (3,815-acre) constructed wetland created by flooding former farm land located at the northwest corner of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge). The details of the layout, vegetative coverage, hydrology, operational regimen, and nutrient removal characteristics of the ENR Project are discussed in Chapter 6 of this report. This section presents a summary of the results of four and one-half years of mercury mass budget studies and bioaccumulation research in the ENR Project from Project startup in August of 1994 to termination in February 1999.

**Appendix 7-5** contains a more detailed summary of the design, methods and results of the mass budget and bioaccumulation studies conducted in the ENR Project supporting these conclusions. The reader is referred to Miles and Fink (1998) and SFWMD (1999) for a more detailed discussion of the mercury mass budget study design, methods, and procedures.

The District began an extensive mercury monitoring and research program in the ENR Project in August 1994. The objectives of this program were as follows:

- Construct annual mass budgets for total mercury and methylmercury to quantify their removal efficiencies
- Evaluate the status and trends of mercury species in water, sediment and biota
- Ensure compliance with Florida Class III Water Quality Standards. An interagency mercury research program was instituted in the ENR Project in July 1995.
- Characterize and quantify the processes, conditions, and factors that govern the pathways and rates of mercury transport, fate, and bioaccumulation
- Develop and parameterize a mechanistic mathematical model of mercury transport-fate-bioaccumulation.

These linked models will be used to predict the local and far-field effects of the ECP on mercury water concentrations, exposures, and risks.

### ENR Mercury Mass Budget Studies

To summarize the results of the ENR Project mercury mass budget study, the ENR Project was a net sink for total mercury and methylmercury, with removal efficiencies for both species calculated to be in the range of 50 percent to 75 percent of the inflow load on an annual average basis. Data gathered on bulk rainfall deposition under the Florida Atmospheric Monitoring Study (FAMS) indicated that almost half of the annual total mercury load to the ENR Project came from wet deposition. Conversely, rainfall was an insignificant source of methylmercury, because it is virtually absent from rainfall. The results of the total mercury and methylmercury mass budget studies are depicted in **Figures 7-8** and **7-9**, respectively.

The District has conducted an analysis of the relationship between total mercury and methylmercury removal efficiencies and ENR Project hydrologic characteristics. These hydrologic characteristics include hydraulic residence time (HRT), inflow pump flow, rainfall depth, and water depth. Based on that analysis, to maximize methylmercury removal efficiency, the ENR Project should be operated to increase the average inflow

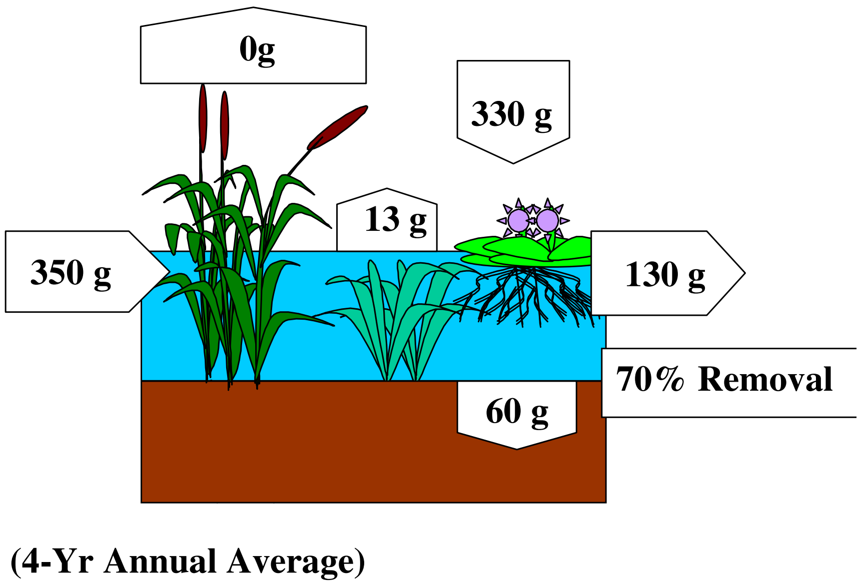


**Figure 7-8.** Total mercury annual average mass budget for ENR Project.

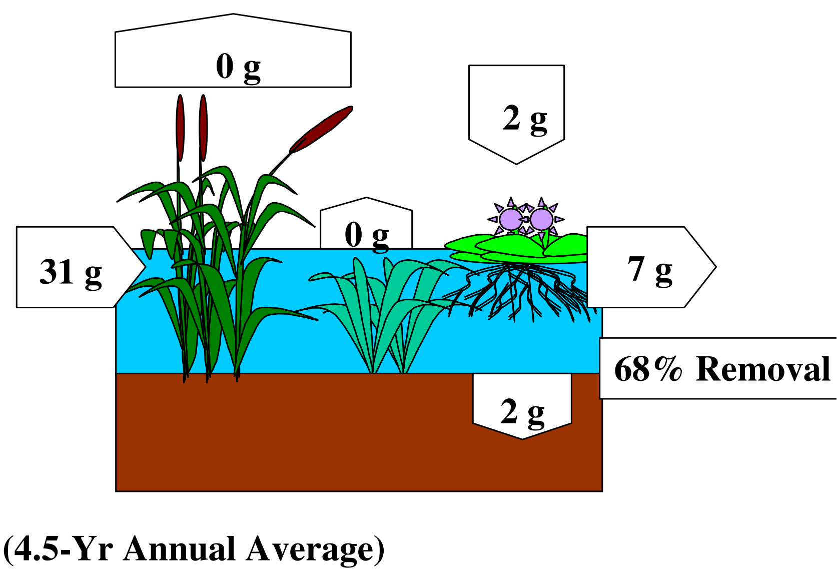


**Figure 7-9.** Methylmercury annual average mass budget for the ENR Project.

pumping rate and water depth during years of high rainfall. Due to the moderate to strong inverse correlation between total mercury removal efficiency and the percent input load from rainfall, such an operating strategy is also likely to increase the total mercury removal efficiency, as well. As the proposed operating regimen for most of the STAs intends to follow this general prescription to maximize phosphorus removal, this should also minimize total mercury and methylmercury discharges to the downstream environment from the STAs.

The most likely mechanism of removal of inorganic mercury and methylmercury from the water column is sorption to settling plant biomass, most likely periphyton and floating macrophyte biomass, which has a much higher surface area and turnover rate than rooted macrophyte biomass. Short-term storage of inorganic mercury and methylmercury occurs in the various submersed above and below ground portions of floating and rooted macophytes and the attached algae mats called periphyton. These short-term storage depots represent less than 10 percent of the throughput of inorganic mercury and methylmercury each year, and the change in storage is less than one percent in most cases, so further effort in monitoring the change in biomass storage would appear to be misplaced. Long-term storage of inorganic mercury occurs in accreting peat soil, which is composed primarily of undecomposed macrophyte tissue. If this is the case, the STAs should be able to sustain this range of total mercury removal efficiencies for the long-term under present-day total phosphorus concentrations and loads in EAA stormwater runoff. However, there is an apparent year-to-year oscillation in the decreasing trend in the concentrations of total mercury in ENR Project sediment that bears further scrutiny.

## Mercury Bioaccumulation Studies

To monitor the status and trends of mercury bioaccumulation in the ENR Project, mosquitofish were collected quarterly at the ENR Project inflow, two interior culverts, eight interior marsh sites, the outflow, and a site upstream of the ENR Project discharge in the adjacent L-7 canal. This was referred to as the L-7 reference site. Largemouth bass were collected annually from at the inflow, one interior site, the outflow, and the L-7 reference site. All species were analyzed for total mercury. Monitoring began in the winter of 1995 and was completed in the winter of 1999. Crayfish were collected at the inflow, two interior culverts, the outflow, and the L-7 reference site using traps from 1995 through 1997. Rather than becoming a mercury "hot spot," the results indicate that the concentrations of total mercury in ENR Project mosquitofish, bass, and crayfish are routinely the lowest found anywhere in the Everglades. Largemouth bass from the interior of Cell 3 never exceeded the state action level of 0.5 ppm and contained only about one-sixth the concentration of total mercury in bass collected in the adjacent L-7 canal. This confirms that there is no reservoir effect developing in the ENR Project overall.

However, beginning in the summer and fall of 1996 and each summer and fall thereafter, the concentrations of mercury in mosquitofish from Cell 4 have been observed to exceed those from Cell 3 by as much as ten times. This pattern is evident in **Figure 7-10**. Having concluded that this pattern was real and persistent, speculation arose that this phenomenon was caused by methylmercury production in the periphyton mats that predominated in Cell 4 but were a lesser component of Cell 3. Methylation in periphyton mats has been observed at some locations in the Everglades (Cleckner et al., 1998). If this were the cause, this might require a reevaluation of Advanced Treatment Technologies (ATT) based on periphyton uptake of total phosphorus in the low concentration range, the so-called periphyton-based STA or PSTA, or modifications thereof, such as the Submersed Aquatic Vegetation (SAV)-Lime Rock system.

To better understand why this difference emerged, the District contracted with outside experts to measure differences in methylmercury production rates in soil and periphyton and differences in food web structure and bioaccumulation patterns. The results of the methylmercury produc-

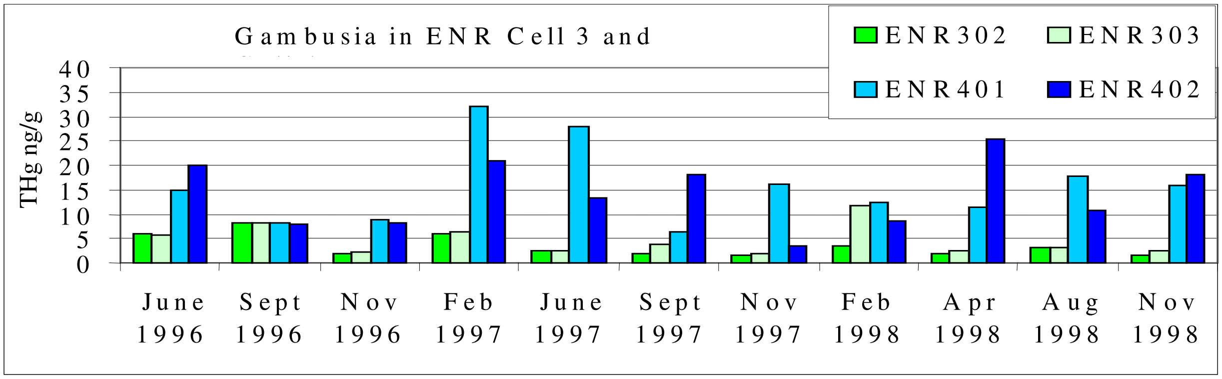


**Figure 7-10.** Total mercury in ENR Project Cell 3 versus Cell 4 mosquitofish over time.

tion studies indicate that the methylation rates of inorganic mercury appear to be higher in Cell 3 than Cell 4 (C. Gilmour, personal communication, 1999), which was an unexpected result. However, primary periphyton habitat made up only 11 percent of Cell 3, but the same habitat made up 93 percent of Cell 4. Consequently, while the methylation rates in Cell 3 may be higher per unit biomass than those in Cell 4, the opposite may be true on a per unit area basis. With the onset of the wet season, the high rainfall rates and concentrations of inorganic mercury combine to substantially increase the loading of potentially bioavailable inorganic mercury to the ENR Project. This increased inorganic mercury load may be more efficiently methylated and less efficiently stored in the submerged macrophyte-periphyton complex in Cell 4 than in the adjacent mixed marsh community in Cell 3. This may explain the difference in the seasonal responsiveness of Cell 3 versus Cell 4.

The differences in methylmercury production alone may not be sufficient to explain the nearly ten-fold peak difference in methylmercury bioaccumulation between Cells 3 and 4. The results of the food web studies indicated that the feeding behavior of mosquitofish were also quite different between cells. Cell 3 mosquitofish stomachs contained an average of 21 percent animal material while stomachs from Cell 4 contained an average of 31 percent animal material (Hurley et al., 1999). Additionally, the distribution of species within the animal material was very different (Hurley et al., 1999). As shown in **Figure 7-11**, Cell 3 mosquitofish had a varied diet of more than eleven taxa, dominated by ostracods, chironimids and rotifers. In comparison, the diet of Cell 4 mosquitofish was limited to six taxa, dominated by dipterans, copepods and leeches.

Interestingly, Rader (1994) identified only one copepod species in the northern Everglades: *Argulus*, a parasite of saltwater fish, freshwater fish, and amphibians (Post, 1983). While it is not believed that *Argulus* is the only copepod species in the Everglades (R. Shuford, SFWMD, personal communication, 1999), if *Argulus* is the dominant copepod in the ENR Project, then by feeding on both copepods and leeches, a significant portion of the Cell 4 mosquitofish diet may be comprised of parasites. This feeding behavior may blur the trophic status of mosquitofish relative to sunfish and bass. Despite apparent increased opportunities for methylmercury exposure, Cell 4 mosquitofish are only about as contaminated as fish at WCA2A-F4, a moderately phosphorus-impacted site. Nevertheless, the District intends to continue to monitor Cells 3 and 4 relative to the L-7 reference site to determine if this trend continues.

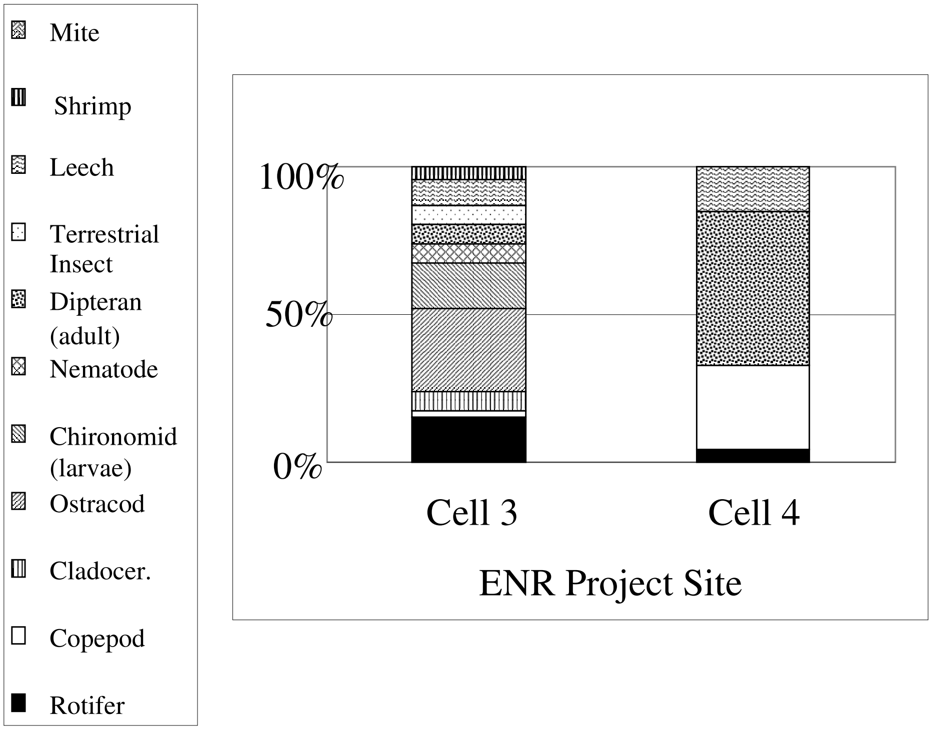


**Figure 7-11.** Differences in the prey preferences between mosquitofish inhabiting Cell 3 vs. those inhabiting Cell 4.

## THE STAS

### Mercury Compliance Monitoring Program

Prior to flooding of the soils of each STA, the District is required to collect and analyze 10-cm core samples of soil at six representative interior sites and analyze them for total mercury and methylmercury. Prior to initiation of discharge, the District is also required to collect biweekly samples of unfiltered inflow and interior water. If the interior water is less than the inflow water, this information is reported to the issuing authority and biweekly sampling ceases. When all the discharge criteria are met, authorization to discharge is obtained and discharge begins. Following approval for initiation of routine operation of each STA and thereafter, unfiltered inflow and outflow samples are collected and analyzed for total mercury and methylmercury quarterly, and inflow, interior, and outflow mosquitofish and largemouth bass are collected and analyzed for total mercury semi-annually and annually, respectively. The sediment coring is also repeated every three years.

### Modeling STA Performance

In addition to quantifying the potential benefits associated with total mercury and methylmercury removal, the unique, self-consistent data sets and mass budgets generated in this study should prove useful in the development and calibration of a mathematical model of mercury transport, biogeochemistry and bioaccumulation in constructed and natural wetlands. The constructed wetlands version of the mercury transport-fate model will be used to maximize phosphorus removal and to minimize inorganic mercury loss and methylation to the extent allowed by the physical, chemical and biological processes that link the phosphorus and mercury cycles. A model capable of meeting this objective, the Everglades Mercury Cycling Model-2, is now under development. The cost of this development is being borne by the USEPA, DEP and the District. A functional version of the model is scheduled to be available for application to the ENR Project in the summer of 2000.

## STA 6

As of this writing, only STA 6 has become fully operational, while pre-flooding baseline samples of soil have been collected from Cell 5 of STA 1W and STA 5. The results of the compliance sampling for water year 1998-1999 are reported in **Appendix 7-2**. Chapter 7 of last year's Everglades Interim Report noted that, on several occasions following start-up, STA 6 outflow concentrations of water or fish exceeded the corresponding inflow concentrations. This unexpected behavior continues in this reporting year.

To put this result in context, a crude mass budget for total mercury was constructed for STA 6. To fill data gaps, water concentrations were linearly interpolated between quarterly sampling events of the inflow and outflow structures, and the actual and interpolated concentrations were multiplied by the corresponding flows for the same periods. To the inflow load was added that from rainfall, calculated by extrapolating the rainfall data being collected at the ENR Project to STA 6. Based on this crude mass budget, STA 6 appears to be a net trap rather than a net source for total mercury, retaining about 50 percent. While there is substantial uncertainty in this result, it is unlikely that STA 6 is a net source of total mercury to the downstream environment, even when the outflow concentrations are apparently higher than the inflow concentrations. This does not appear to be the case for methylmercury, however, and it has been speculated that this difference may be caused by the frequent periods of drying and reflooding followed by extended periods of standing water. Both of these conditions are believed to contribute to enhanced methylmercury production, accumulation, and bioaccumulation. Because shallow-water conditions in the STAs can attract wading birds, it is appropriate to consider the potential methylmercury exposures and risks to wading birds feeding exclusively in STA 6.

To do this, a probabilistic ecological risk assessment was conducted for the Great Blue Heron, because it is the species that generates the consistently highest risk estimates, i.e., the worst-case species. This is because it tends to take the largest fish. Only limited data are available on the concentrations of methylmercury in largemouth bass in STA 6 from an annual collection in the fall of 1998. The ecological risk assessment was conducted with two exposure scenarios. The first involved the assumption that 100 percent of the diet was juvenile largemouth bass in the appropriate size range. The second scenario involved a prey preference weighted average diet made up of juvenile largemouth bass, warmouth, other sunfish species and golden shiners. Because only largemouth bass and mosquitofish are collected for permit compliance at the STAs, the concentrations of methylmercury in warmouth and other sunfish species were estimated from measured ratios between those species and bass using data from all other sites in the database. The golden shiner methylmercury concentrations were assumed equal to those of the mosquitofish, although usually mosquitofish concentrations are higher, so this assumption intentionally biases the exposure estimate high. The No Observable Adverse Effect Level (NOAEL) for methylmercury in wading birds is then approximated by multiplying the Mallard Duck Lowest Observable Adverse Effect Level (LOAEL) by a factor of 0.5. The hazard quotient was then calculated as the ratio of the estimated daily intake rate to the Mallard Duck No Observable Adverse Effect Level. The results indicate that median and 95$^{th}$ percentile upper bound hazard quotients for the Great Blue Heron feeding on a more typical mix of fish species is 1.3 and 2.4, respectively, while the median and 95$^{th}$ percentile upper bound hazard quotients for a diet consisting solely of juvenile bass are 2.65 and 4.4, respectively.

To put these risk estimates into perspective, the WCA-3A-15 site is often used as a benchmark representing the threshold of concern for methylmercury risks to wading birds, although the corresponding population-level impacts have not been observed in the highly exposed populations colonizing the area (**Appendix 7-3b**). Based on the fact that the median and 95$^{th}$ percentile upper bound hazard quotients for the Great Blue Heron feeding with typical prey preferences at STA 6 are lower than those calculated for WCA-3A-15, there should be no expectation of population-level effects in any wading bird subpopulation feeding exclusively in STA 6.

However, where the protection of individual animals is at issue, as is the case with endangered species like the wood stork, there is a possibility of some members of the subpopulation feeding exclusively in STA 6 to experience some methylmercury toxic effects if they are as sensitive to or more sensitive than the Mallard Duck. This concern can be relaxed somewhat by recognizing that it is highly unlikely that any wading bird subpopulation will feed exclusively at STA 6. Nevertheless, the purpose of such an ecological risk assessment is to set priorities for more focused attention. The District has conducted appropriate follow-up studies, although outside the reporting period.

In the first study, the District collected fish from both sides of the supply and discharge canal structures to evaluate the potential for and source of fish population mixing among inflow, interior and outflow populations. The preliminary results indicate that the inflow and outflow fish populations are mixing via the L-4 canal, but the interior populations are distinct. In second study, the District obtained samples of STA 6 sunfish from Ted Lange of the Florida Game and Wildlife Conservation Commission, although such collections are not now required in the federal or state permits to construct and operate STA 6. These sunfish will be analyzed for total mercury and the results used to refine the wading bird ecological risk assessment for STA 6.

The data from these fish collections are not yet available, but both sets of results will be reported to DEP, USEPA, and the Corps as soon as they have completed quality assurance to ensure that any potentially ecologically significant risks to fish-eating birds will not have to await the preparation of next year's Everglades Consolidated Report. Should any of the permitting authorities conclude that the risks presented by normal operation of STA 6 to endangered species like the wood stork are unacceptable, options for manipulating the hydrology to exclude wading birds will be evaluated. However, the ultimate solution to the problem is the reduction of inorganic mercury concentrations in rainfall through source control, and not the manipulation of water quantity or quality to limit exposures or modify the assimilative capacity of the receiving water body.

The potential methylmercury exposure concerns raised by STA 6 may extend to water bodies with similar soil and drying/reflooding characteristic that are receiving roughly the same annual supplies of inorganic mercury from storm runoff and rainfall. Such water bodies could include residential, commercial and agricultural swales for storm runoff capture and treatment, which routinely dry out and then reflood with ponding of water for extended periods. Such swales attract wading birds, and wading bird subpopulations feeding exclusively or preferentially in those water bodies could be at elevated methylmercury risks.

### STA 1W

Cell 5 of STA 1W is similar in all respects to ENR Project Cells 1 and 2, with the exception of its pre-flooding preparation and timing of flooding. However, each of the ENR Project cells was harvested, plowed, and treated with herbicides to limit the invasion of undesirable plants like torpedo grass prior to flooding, but the unharvested last sugar cane crop remained standing in the field after Cell 5 flooding. This is a source of fresh decomposing biomass that was unavailable to the microbes in the ENR Project at start-up. In addition, much of the ENR Project was first flooded in the late summer through the late fall, which meant that its pre-operational incubation period occurred primarily in the winter and spring when the inorganic mercury load from rainfall was low and temperatures were cool. Conversely, Cell 5 was flooded in the spring of 1999 and began pre-operational incubation in the early summer, when rainfall inorganic mercury loads and temperatures were increasing to a seasonal maximum in August. Although start-up sampling of STA 1W did not commence until the close of water year 1998-1999, the preliminary results are sufficiently noteworthy that they bear reporting now.

In June 1999, unfiltered total mercury and methylmercury concentrations in pre-operational Cell 5 peaked at about ten times and about 30 times, respectively, those typical of the ENR Project interior over the previous four years. Follow-up sampling of interior Cell 5 mosquitofish found a mean concentration of about 100 ng/g. As of this writing, both water and mosquitofish concentrations have decreased by about 50 percent from the observed peak. By contrast, mosquitofish collected in adjacent Cell 4 were running about 2.5 ng/g, or 5 percent of the Cell 5 mosquitofish. As of this writing, the mercury start-up criteria have not been met for STA 1W. The details of the results of the pre-operational sampling of Cell 5 will be left to next year's Everglades Annual report to ensure that the entire set of results is available to put it into proper perspective.

## EVERGLADES CONSTRUCTION PROJECT: LONG-TERM ASPECTS

The target total phosphorus concentration in treated EAA runoff in Phase 2 of the ECP is 10 ppb or the new numerical Class III Water Quality Standard for total phosphorus if it is promulgated before December 31, 2001. The Phase 2 treatment strategy will continue on-farm BMPs but will add Advanced Treatment Technologies (ATT) to the inflow, interior or outflow of the STAs. The candidate ATTs include Submerged Aquatic Vegetation (SAV) and Lime Rock, Periphyton-Based STA (PSTA) or Porta-PSTA, Chemical Addition, Managed Wetlands, and hybrids like Chemical Addition with Solids Separation and Chemical Addition with Managed Wetlands. The ATT Program and the individual ATT projects are discussed in greater detail in **Chapter 8**.

It is not known *a priori* whether any of the candidate ATTs will perform like the ENR Project with respect to inorganic mercury removal and storage and methylmercury production, removal, storage and bioaccumulation. However, where the design calls for the addition of chemicals known or reasonably expected to stimulate inorganic mercury methylation (e.g., ferric sulfate or long contact times between periphyton species know or reasonably expected to foster inorganic mercury methylation (e.g., *Spyrogyra*), mercury screening studies are certainly justified.

Methylmercury production in Everglades periphyton was measured by Cleckner et al., 1999 by spiking with an inorganic mercury radioisotope (203-Hg(II)). In addition, methylation of inorganic mercury has been measured in the microbial communities living in the roots of floating macrophytes collected from the ENR Project, including *Azola sp*., *Eichhornia crassipes* and *Pistia sp.* (Mauro and Guimaraes, 1999) or inferred from the association of methylating communities with other sulfur bacteria with distinct pigment signatures (Hurley et al., 1999). In each case, the methylation of mercury appears to be mediated by sulfate-reducing bacteria (SRB). Evidence in support of this conclusion comes from the quantitation of methylmercury production with the addition of sulfate reduction inhibitors, additions of methanogen inhibitors, and the presence of bacteriochlorophyll a (Gilmour et al., 1998a; Cleckner et al., 1999; Hurley et al., 1999). While these favorable habitats can facilitate methylation of inorganic mercury under favorable conditions, attention must also be paid to the relative abundances of these favorable habitats before drawing conclusions about the magnitudes of their influences on methylmercury production and bioaccumulation at a specific locale. For example, in the ENR Project the assumption that virtually 100 percent of its surface area is covered with peat soil is justifiable, but in 1998, 41 percent and 4 percent of the Project's 1491 acres were classified as open water/algae-macrophyte complex and floating macrophytes, respectively (SFWMD, 1999). Thus, while it is appropriate to quantify the contribution of the algae-macrophyte complex to methylmercury production and bioaccumulation in the ENR Project, such effort would appear misplaced for floating macrophytes. If these same proportions hold in the large-scale ATTs, then same conclusion applies.

To ensure that the ATTs will not generate significant quantities of methylmercury or concentrate inorganic mercury or methylmercury to hazardous levels in solid residues, a screening-level monitoring study is planned. Within the ENR Project are two banks of 15, side-by-side, miniature filter marshes (approx. 0.5 acres each) referred to as test cells. One bank is at the north end of Cell 1 in the ENR Project, where water total phosphorus concentrations are about 100 ppb, and the other is at the north end of Cell 3, where total phosphorus concentrations are in the range of 50 ppb. Originally designed to optimize total phosphorus removal in the STAs, the test cells are now being adapted to the screening and optimization of the candidate ATTs. A $150,065 Section 319 Grant has been awarded to the District to offset most of the cost of ultra-trace total mercury and methylmercury analyses and some labor costs for the screening study during the standards of comparison phase of the ATT test cycle.

## Potential Downstream Mercury Impacts of the ECP

During the environmental impact assessment and permitting phases for the STAs, concerns were raised by the Sugar Cane Growers Cooperative of Florida (Cooperative) that the changes in the downstream water and sediment chemistry to be brought about by the STAs would exacerbate the existing mercury problem in the Everglades. Support for this concern was contained in a report prepared by PTI (now Exponent) for the Cooperative. The report claimed to demonstrate the existence of an inverse relationship between eutrophication (quantified as water column total phosphorus) and methylmercury in mosquitofish (PTI, 1995a,b). This relationship was derived using District water chemistry data and USEPA mosquitofish mercury data collected along a nutrient gradient south of the S-10 structures in WCA-2A (USEPA, 1998). PTI/Exponent proposed two primary mechanisms to explain the apparent inverse relationship between water column total phosphorus and methylmercury in mosquitofish: (1) increased removal of inorganic mercury and methylmercury from the water column sorbed to settling plant biomass and (2) dilution of the remaining mercury species in the increased production of plant biomass and accumulating peat. The report (Exponent, 1998) was revised, expanded and submitted on behalf of the Cooperative for the consideration of last year's Peer Review Panel.

In Chapter 7 of last year's Everglades Interim Report, the District conducted an extensive and detailed analysis of the potential positive and negative effects of phosphorus reduction from the ECP on the downstream mercury problem in the Everglades. That analysis was presented on pages 7-38 to 7-49 and in Appendices 7-2, 7-3 and 7-4. Based on that analysis, the District concluded that it was highly unlikely that the reduction of water column total phosphorus to 10 ppb in the already impacted areas would cause or contribute to an ecologically significant increase in methylmercury exposure and toxic effects in any wading bird population feeding exclusively in the already impacted areas after remediation. The District pursued three separate approaches in arriving at that conclusion.

**Reference Site Approach.** Evaluate the pre-STA mercury risks at an unimpacted reference site to approximate post-STA conditions in the already impacted area. Compare these risks to those at the most contaminated site as a positive control. The reference site selected for this purpose was WCA-2A-U3, where water column total phosphorus concentration already averages less than 10 ppb, but where hydrology and water chemistry were otherwise very similar to those in the already impacted area. Validate exposure and toxicity estimates against field observations. Use the validated exposure and toxicity assumptions to predict post-STA mercury risks.

**Statistical Modeling Approach.** Measure mercury in water, sediment, plants and wildlife along with related water and sediment chemistry data at various Everglades sites to identify important influential factors using various statistical models. Test the predictive validity of these statistical models against real conditions at other sites in the Everglades. Use the validated statistical models to predict post-STA mercury risks.

**Mechanistic Modeling Approach.** Quantify the key processes and influential factors that govern methylmercury production and bioaccumulation in controlled experiments in the laboratory and field. Develop a mathematical model that includes all of these processes and influential factors in a realistic way. Fill key data gaps with literature values until Everglades-specific results become available. Test the validity of this realistic mathematical model against real conditions in other portions of the Everglades. Use the validated mechanistic model to predict post-STA mercury risks.

The results of all three approaches were summarized in Chapter 7 of last year's Everglades Interim Report. The first approach was conducted in Appendices 7-2 and 7-3, while **Appendix 7-4** presented the second and third approaches.

Based on the first approach, the District concluded that it is highly unlikely that there will be an unacceptable increase in post-STA methylmercury risks to fish-eating birds. When the exposure estimates prepared for the Sugar Cane Growers Cooperative (Exponent, 1998) were corrected with Everglades-specific data, the two risk assessments were in substantial agreement. This correction analysis was conducted in Appendix 7-3 of last year's Everglades Interim Report. The District's probabilistic ecological risk assessment included as **Appendix 7-3b** of this chapter reinforces last year's results and conclusions.

The results of the second approach revealed that there are a number of factors that could be influencing methylmercury production and bioaccumulation along the nutrient gradient in WCA-2A and elsewhere in the Everglades. The strongest influences on methylmercury production in the sediment appear to be pore water sulfide and total mercury in peat soils, while the strongest influences on methylmercury bioaccumulation along the WCA-2A nutrient gradient appear to be dissolved organic carbon (DOC), hardness and total phosphorus in the water column. However, it was concluded in Chapter 7 of last year's Everglades Interim Report that neither the District's two-variable statistical model based on water column DOC and calcium nor the one-variable statistical model based on water column total phosphorus developed for the Sugar Cane Growers Cooperative were valid for predicting post-STA mercury risks. This is because neither could accurately predict methylmercury bioaccumulation in mosquitofish at other Everglades sites using the appropriate water quality data. The results of this year's multivariate analysis of the influences of water and sediment chemistry on methylmercury bioaccumulation support last year's results and conclusions.

The third approach used a mathematical model built by USEPA's Office of Research and Development. It included everything that was known up to 1998 about methylmercury production and bioaccumulation in the Everglades, including the influence of water column total phosphorus on plant production and decomposition and the accumulation of undecomposed plant matter called peat. These are the key elements of biodilution. The results of the pre- and post-STA modeling analysis indicated that there could be some (about 50 percent) but not an ecologically significant increase in methylmercury bioaccumulation in the already impacted area. Further, there was a benefit to the reduction in post-STA mercury loads to the northern Everglades. Thus, there is likely to be a substantial margin of safety in the results of the first approach, which is based on a 10-fold increase in methylmercury bioaccumulation between WCA-2A-F1 and WCA-2A-U3.

For a discussion of the influences of water quantity and quality on the Everglades mercury cycle, the reader is referred to the section titled: The Role of Phosphorus in Mercury Cycling in Aquatic Ecosystems in Chapter 7 of last year's Everglades Interim Report (pp. 7-20 to 7-24) for a summary of the known and potential influences of phosphorus on the Everglades mercury cycle and to the sections titled: Managing Methylmercury Production and Transport through Hydrological Controls, Managing Methylmercury Exposure through Hydrological Controls, and Managing Methylmercury Production and Bioaccumulation through Water Quality Controls (pp. 7-32 to 7-35). In what follows, the focus is on new information regarding the roles of phosphorus, sulfur and hydrology in determining methylmercury production and bioaccumulation along the WCA-2A nutrient gradient.

### The Inverse Relationship with Phosphorus

The inorganic mercury and methylmercury transported into or generated within the marsh have a high affinity for organic solids (Hurley et al., 1998; Mason and Lawrence, 1999). As the plant leaves and algae cells making up the periphyton mat die and slough off, the inorganic mercury and methylmercury sorbed to their surfaces is carried into the plant litter complex accumulating at the soil/water interface (Araujo and Ambrose, 1999). Over a number of years, the consolidating undecomposed plant litter becomes peat soil. The high affinity for inorganic mercury for the organic matter in peat soil tends to limit its release, mobility and activity. This also tends to preserve the history of the inorganic mercury deposition rate in the peat soil profile. If the layers of the sediment can be dated, this allows a reconstruction of the historical inorganic mercury deposition rate (Delfino et al., 1993; Benoit et al., 1994; J. Robbins, NOAA-GLERL, personal communication, 1997).

As a general observation for lakes, where plant production and sedimentation are high, methylmercury bioaccumulation in the aquatic food chain is low and vice versa (D'Itri, 1971; Hakanson, 1980). The term applied to this phenomenon is "biodilution." Biodilution occurs when the supply of inorganic mercury or methylmercury remains relatively constant but the production of plant biomass increases. All other things then being equal, the concentration of inorganic mercury or methylmercury in the plant biomass decreases, because the constant fluxes of mercury species sorbed to plant cell surfaces are diluted in the increased plant biomass production. In addition, the higher the rate of plant biomass production, the higher the rate at which sorbed inorganic mercury and methylmercury are removed from the water column through settling of plant litter and the eventual burial in the accumulating peat soil. The dilution in the standing crop of plant biomass and the increased settling rate can be considered the primary effects of biodilution. The increase in peat production in response to an increase in phosphorus has the net effect of diluting the inorganic mercury in accumulating peat soil. This has been observed along the WCA-2A nutrient gradient (Delfino et al., 1993; Vaithiyanathan et al., 1996; USEPA, 1998). This is another manifestation of the primary effect of biodilution.

The lower concentrations of methylmercury in the plant standing crop are then biomagnified by plant grazers, their predators and so on up the food chain. This transfers the biodilution effect to all trophic levels in the aquatic food chain. In addition, some scientists have argued that where the rate of growth of fish is limited by the availability of prey, and the availability of prey is limited by the availability of live or decomposing plant biomass, then higher plant production should result in more rapid fish growth and a dilution of the methylmercury being taken up via the gut by accumulating body mass. This could be considered a secondary effect of biodilution. However, fish growth can also be controlled by other factors like the length of time the water remains depth enough for a fish to forage successfully for its preferred prey (T. Lange, FGWCC, personal communication, 1997), the density of the fish population, the general quality of the water or the presence of pollutants that slow or stunt growth.

As this plant litter decomposes, some of the sorbed inorganic mercury and methylmercury is released back into the water column to participate in other chemical and biochemical reactions, while the rest remains in association with the decomposing and consolidating litter. The bacterial cells growing on the decomposing plant litter generally have higher surface area-to-volume ratios than algal cells and thus tend to outcompete them for inorganic mercury and methylmercury (C. Miles, UF, personal communication, 1999). This suggests that the distinction between autotrophic and saprotrophic grazers is important in determining the biomagnification at the next step in the food chain.

The decomposition of plant matter also produces aggregates of small molecules called humic and fulvic acids. These substances impart the tea color to productive, slow moving waters. These substances also have a high affinity for inorganic mercury and methylmercury (Aiken and Reddy, 1997) and can outcompete algal cell surfaces for these species. Dissolved organic carbon has been demonstrated to outcompete algal cell surfaces for copper ion over a wide range of pH (Plette et al., 1999), and, in general, inorganic mercury has a higher affinity for dissolved organic carbon than copper. All other things being equal, high concentrations of dissolved organic matter are associated with lower concentrations of inorganic mercury and methylmercury bound to plant cell surfaces and vice versa. This inverse relationship between the concentration of dissolved organic matter and methylmercury bioconcentration in microscopic plants and animals has also been observed to translate up the food chain in seepage lakes (Grieb et al., 1990; Watras et al., 1994). In drainage lakes, dissolved organic matter is positively correlated with methylmercury bioaccumulation, probably via enhanced transport of methylatable inorganic mercury from the watershed into the system (Grieb et al., 1990).

The affinity of live, dead and dissolved organic matter surfaces for inorganic mercury and methylmercury can be influenced by water chemistry. The hydrogen ion activity (as measured by pH) is perhaps the strongest determinant of speciation, fractionation and reaction of metals in natural waters (Sposito, 1998) and of methylmercury bioaccumulation (Winfrey and Rudd, 1990). Inorganic mercury and methylmercury are generally believed to be most strongly bound to the reduced sulfur binding sites in humic and fulvic macromolecular complexes (Xia et al., 1999). However, the number of such sites on humic or fulvic acid fractions is generally small relative to the carboxyllic and phenolic binding sites (Xia et al., 1999), and access to reduced sulfur binding sites may be limited due to the tendency of the molecule to present its carboxyllic and phenolic binding sites to maximize hydrogen bonding opportunities with water. In this way, the inorganic mercury and methylmercury may first interact with the network of weaker binding sites until they can break free and diffuse deeper into the structure until a reduced sulfur binding site is encountered.

If this is the case, then other “hard” divalent cations can also strongly influence the sorption of inorganic mercury and methylmercury to plant cell surfaces and dissolved organic matter via competition for binding sites, altering cell surface electrostatic properties or altering the ionic strength of the solution (G. Aiken, USGS, personal communication, 1999), as is observed with mineral surfaces (Sposito, 1998). For example, at moderate to high concentrations of calcium and magnesium, some of the caroboxyllic and phenolic binding sites on the dissolved organic matter may be occupied, precluding binding with mercury. The presence of moderate to high concentrations of calcium and magnesium may also change the conformation of the aggregate (Maurice and Namjesnik-Dajanovic, 1999), which can increase or decrease access to interior biding sites, or change the surface charge of the aggregate, limiting the electrostatic attraction of those surfaces for mercury (Engebretson and Von Wandruzka, 1998). Copper also has a high affinity for humic binding sites (Robertson and Leckie, 1999). With copper present in concentrations three orders of magnitude higher than inorganic mercury and four orders of magnitude higher than methylmercury, copper may outcompete inorganic mercury or methylmercury for carboxyllic and phenolic binding sites and perhaps even the sulfhydryl binding sites, at least for some period of time (G. Aiken, USGS, personal communication, 1999).

Is phosphorus-mediated biodilution occurring in the Everglades? Will a reduction in water column phosphorus in the already impacted area to 10 ppb cause an associated reduction in biodilution that results in an unacceptable increase in methylmercury bioaccumulation in fish? To answer this question, an analysis was conducted on the available data collected by the District on plant densities and production rates and by the USGS ACME team on the concentrations of total mercury associated with each plant type. If classical biodilution is occurring along the WCA-2A nutrient gradient, then the concentrations of total mercury and methylmercury will be lower in the water column, sediment, plants and fish at F1, the most nutrient-enriched or eutrophic site, and highest in the water column, sediment, plants and fish at U3, the unimpacted reference site where nutrient-poor or oligotrophic conditions prevail. Certainly water, sediment and fish concentrations all increase with downstream distance along the nutrient gradient, suggesting a strong biodilution effect. However, the plant data are not so compelling.

The study sites along the WCA-2A nutrient gradient are depicted in **Figure 7-12.** A calculation of the magnitude of biodilution for total mercury was conducted for macrophytes (cattail and sawgrass) and periphyton species at four sites along the nutrient gradient: F1, E1, U3 and U1. The spatially weighted-average plant production was calculated by multiplying the spatial coverage of each plant by the corresponding plant density and the plant production or turnover rate (McCormick et al., 1998; Miao and Sklar, 1998). The total mercury concentration in each plant type (D. Krabbenhoft, USGS, unpublished data, 1999) was then multiplied by its appropriate spatially-weighted average turnover rate to obtain the total mercury flux through each plant type. The results of the macrophyte and periphyton storage and turnover calculations are displayed in **Table 7-1**.

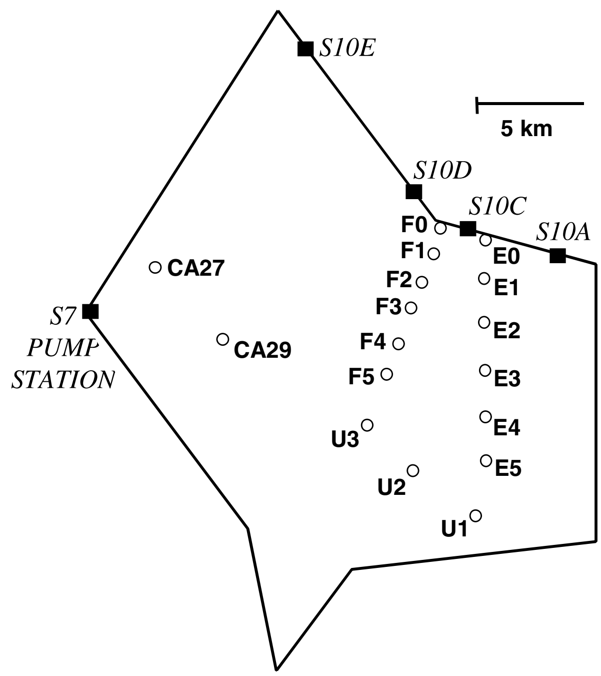


**Figure 7-12.** Research sites located along nutrient gradient in WCA-2A

As expected, macrophyte density, production and turnover are higher at the eutrophic sites, as is the total mercury cycled through macrophyte biomass. Macrophyte cycling of total mercury through macrophyte biomass decreased by 35 percent while the total mercury concentration more than tripled, so the macrophytes are behaving at least qualitatively like what would be predicted by the biodilution hypothesis. However, due to the low concentrations of total mercury in macrophyte biomass, the quantity of total mercury being cycled through plant biomass (7-10 $\mu g/m^2$-yr) is small compared with the estimates of the combined wet and dry deposition flux to the Everglades (35 to 45 $\mu g/m^2$-yr). The corresponding average flux of total mercury from the sediment has been observed to be negative, that is, the overlying water is usually sat-

**Table 7-1.** Primary producer biomass, THg concentrations and flux rates under a high and low nutrient regime

| Sites | Coverage-Weighted Biomass (g dry/$m^2$) | THg (ng/g dry) | THg Storage (ng/m2) | Plant Biomass Turnovers Per Year (g dry/g dry-yr) | THg Cycled Through Plant Biomass (ug/$m^2$-yr) |
|---|---|---|---|---|---|
| Eutrophic Sites | | | | | |
| Macrophytes | 920 | 2.1 | 1900 | 5.0 | 9.5 |
| Periphyton | 1.4 | 205 | 280 | 150 | 42 |
| Oligotrophic Sites | | | | | |
| Macrophytes | 520 | 6.7 | 3500 | 2.0 | 7 |
| Periphyton | 370 | 39 | 14,400 | 9.1 | 130 |

urated with total mercury relative to the pore water in peat soil (G. Gill and co-workers as discussed in Gilmour et al., 1998b). So the throughput and cycling of total mercury through plant biomass is probably being driven primarily by atmospheric deposition. In addition, some, perhaps a substantial fraction of the total mercury in macrophyte leaves and stems could originate with the soil and be recycled directly back to the soil without ever participating in any of the other mercury biogeochemical processes leading to methylmercury production.

Perhaps surprisingly, the coverage-weighted periphyton biomass was more than two hundred times higher at the oligotrophic sites than the eutrophic sites, resulting in a mercury flux through periphyton biomass at the oligotrophic sites three times that at the eutrophic sites. This is the opposite of the relationship expected for biodilution mediated by water column phosphorus. Consistent with the greater turnover of periphyton at the oligotrophic sites, the total mercury concentrations at the oligotrophic sites were one-fifth those at the eutrophic sites. Despite the lower total mercury concentration, the oligotrophic periphyton stored nearly 40 times more total mercury in standing crop biomass per unit area than the eutrophic site. In addition, the turnover of total mercury through periphyton biomass at the eutrophic site is about equal to the annual average wet and dry deposition flux of inorganic mercury to the Everglades, while that at the oligotrophic site is about four times that value. This strongly suggests that periphyton is only a temporary storage depot for inorganic mercury and methylmercury and that a substantial portion of the total mercury sorbed to periphyton biomass is returned to the water column during biomass decomposition; otherwise, there would be no way to sustain the calculated total mercury turnover rate at U3 without an external deposition flux of total mercury that would be inconsistent with the peat accretion profile (Delfino et al., 1993).

Based on the preceding analysis, it is clear that the oligotrophic site has a higher biodilution factor than the eutrophic site, contrary to the phosphorus-mediated, classical biodilution hypothesis. This counterintuitive result probably arises from the suppression of periphyton production through light limitation (Grimshaw et al., 1997). Light limitation occurs at the highly eutrophic sites because the dense canopy of living and dead emergent macrophyte biomass shades the water column. Grimshaw et al., 1997, found a significant decrease in net primary production of periphyton under *Typha* stands when compared to open waters and *Cladium* stands. As a result of light limitation, the "classical" link between eutrophication and biodilution is broken and is no longer directly applicable to the more eutrophic sites along the WCA-2A nutrient gradient. The net result of this light limitation effect is that the greater standing crop density and higher turnover rate of plant biomass is occurring at the oligotrophic site (McCormick et al., 1998), and this is apparently resulting in lower concentrations in plant biomass than at F1, despite the fact that the concentration of total mercury in the surrounding water is higher on average at U3 than at F1.

The expected relationship between biodilution and eutrophication appears to be present in the macrophyte community. Macrophyte biomass is greater and the calculated mercury turnover rate is higher at the eutrophic site than at the oligotrophic site. In addition, the concentration of total mercury appears to increase in peat soil as water column phosphorus decreases (Delfino et al., 1993; Vaithiyanathan et al., 1996), suggesting that the rate of peat formation and dilution of the rainfall mercury flux increases as water column phosphorus increases. This is a weaker manifestation of the primary biodilution effect. Due to the apparent relationship between soil total mercury and methylmercury production and bioaccumulation, this manifestation of the biodilution effect must be taken into account in any complete and accurate conceptual or mathematical model of mercury cycling in the Everglades. This manifestation of the biodilution effect is taken into account by the USEPA-ORD model.

Based on the light limitation effect occurring along the WCA-2A nutrient gradient, classical biodilution cannot be the explanation for the observed inverse relationship between water column total phosphorus and methylmercury bioaccumulation in mosquitofish along the WCA-2A nutrient gradient. The apparent inverse relationship between water column total phosphorus and methylmercury bioaccumulation in mosquitofish is correlation, not causation.

There are two alternative explanations for the apparent inverse relationship between water column total phosphorus and methylmercury bioaccumulation in mosquitofish. The first alternative explanation is based on the sulfur hypothesis: (1) methylmercury bioaccumulation is determined primarily by the net production of methylmercury in peat soil, (2) the rate of methylmercury production is determined by its inverse relationship with pore water sulfide, and (3) it is the decreasing pore water sulfide gradient along the WCA-2A nutrient gradient that is causing methylmercury production to increase with increasing distance downstream of the S-10 discharges. The second alternative explanation is based on the flow dilution hypothesis: (1) the concentrations of total mercury and methylmercury in the S-10 flows are lower than in the marsh, (2) as the S-10 plume enters the marsh, it slows and spreads and mixes with the surrounding WCA-2A water and the inorganic mercury flux in rainfall, (3) this results in an increase in the total mercury and methylmercury concentrations with downstream distance until the plume and marsh waters are completely mixed. Both alternatives are discussed below.

### The Inverse Relationship With Sulfide

Some but not all of the inorganic mercury sorbed at the surface of the decomposing plant litter is available for transport or chemical or biochemical reaction. Methylmercury is produced from a bioavailable pool of inorganic mercury by sulfate-reducing bacteria under anoxic conditions (Gilmour and Henry, 1991). While dissolved sulfate stimulates SRB activity up to a point (Gilmour et al., 1992), its absence is not always associated with inactivity by SRB (C. Gilmour, ANS, personal communication, 1999). Plant biomass breakdown by fermentative bacteria supply short-chain organic acids required by the SRB (W. Orem, USGS, personal communication, 1999). In carbon-limited systems, the higher the fraction of organic matter in the sediment, the higher the rate of methylmercury production (Olson and Cooper, 1976). However, it is unlikely that carbon limits SRB activity or methylmercury production in the Everglades (M. Marvin-DiPasquale, USGS, pers comm., 1999). Although nitrate-reducing bacteria have been shown to outcompete SRB for the same carbon source under certain conditions in other aquatic systems, this has not been demonstrated to occur in the Everglades (C. Gilmour, ANS, personal communication, 1999). The maximum methylation rates occur in a zone between two and four cm below the sediment/water interface, where DO is absent but supplies of sulfate and carbon are abundant (Gilmour et al., 1998b).

Microbial methylmercury degradation represents a primary control on the net production of methylmercury in sediments (Marvin-DiPasquale and Oremland, 1998). Aerobic bacteria, SRB and methanogens can all demethylate methylmercury (R. Oremland, USGS, personal communication, 1997). Spatial trends in methylmercury degradation typically parallel those of inorganic mercury methylation (Marvin-DiPasquale and Oremland, 1998), suggesting that the conditions that favor microbial methylation also favor demethylation and vice versa. The maximum rate of demethylation typically occurs at or near the sediment surface and decreases with depth. These spatial trends in rates of microbial inorganic mercury transformation reflect both the bioavailability of the inorganic mercury or methylmercury substrate and the activity of the microbial community at a given location (M. Marvin-DiPasquale, USGS, personal communication, 1999).

Methylmercury can also be decomposed to inorganic mercury or elemental mercury by a photoxidative process for which sunlight provides the energy (Sellers et al., 1996). Methylmercury complexed with dissolved organic matter may be shielded from this effect, while elemental mercury production from inorganic mercury complexed with dissolved organic matter may be enhanced (S. Lindberg, ORNL, pers comm., 1998). Conversely, dissolved organic matter may also facilitate the production of hydroxyl radicals that participate in the oxidation of elemental mercury to inorganic mercury (Vaughn and Blough, 1998). However, the dissolved organic matter also absorbs the photo active wavelengths of sunlight, so the highly colored waters of the Everglades preclude much photochemistry below a few cm beneath the water surface (D. Krabbenhoft, USGS, personal communication, 1997; S. Lindberg, ORNL, personal communication, 1998).

As depicted in **Figures 7-13 and 7-14,** there appears to be a moderate inverse correlation of methylmercury in Everglades soils with peat pore water sulfate, but a much stronger inverse correlation with peat pore water sulfide (C. Gilmour, ANS, personal communication, 1999).

According to Benoit et al. (1999 a, b), the mechanism by which sulfide exerts its negative influence on methylmercury production may be via the formation of charged sulfide complexes of inorganic mercury that cannot cross the cell membrane of the sulfate-reducing bacteria (*Desulfovibrio* species). Iron may also play a role in this process by forming polysulfide complexes that could stimulate or retard methylmercury production, depending on conditions (C. Gilmour, ANS, personal communication, 1997).

As depicted in **Figure 7-15**, the transport of excess sulfate from the EAA and sites of excess of sulfate in water and sediment downstream has been inferred from the unique sulfur isotope signature of EAA runoff sulfate relative to those of rainfall, Lake Okeechobee water, and groundwater (Bates et al., 1998). The influence of the excess sulfate from the EAA extends into WCA-3A (**Figure 7-16**). In addition, the vertical accumulation of sulfate in the sediment horizon downstream of the EAA, even as far as the headwaters of Taylor Slough, suggests that recently deposited sulfate exceeds natural background by many times (**Figure 7-17**).

If the sulfur hypothesis is correct, first an increasing and then decreasing (parabolic) relationship should exist between the concentration of sulfate in the peat soil pore water and net methylmercury production. If such a parabolic relationship exists in the Everglades, then there must be a location where the conditions for net methylation are at the peak of the parabola, and the net methylmercury production rate and concentrations in sediment, water and biota are all at a maximum. That location is believed to occur in the central portion of WCA-3A near WCA-3A-15. In this area, the ratio of sulfide to sulfate in peat pore

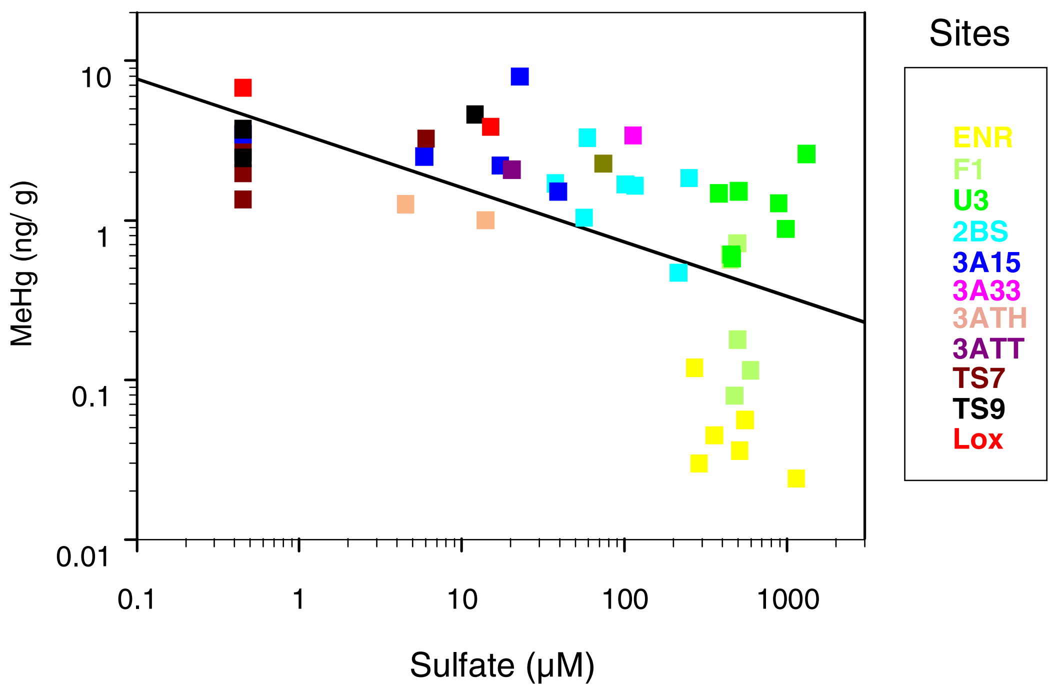


**Figure 7-13.** Sulfur cycle influences on methylmercury in Everglades peat soils: sulfate (Reproduced with permission by Cynthia Gilmour, Ph.D., ANS, St. Leonard, MD).

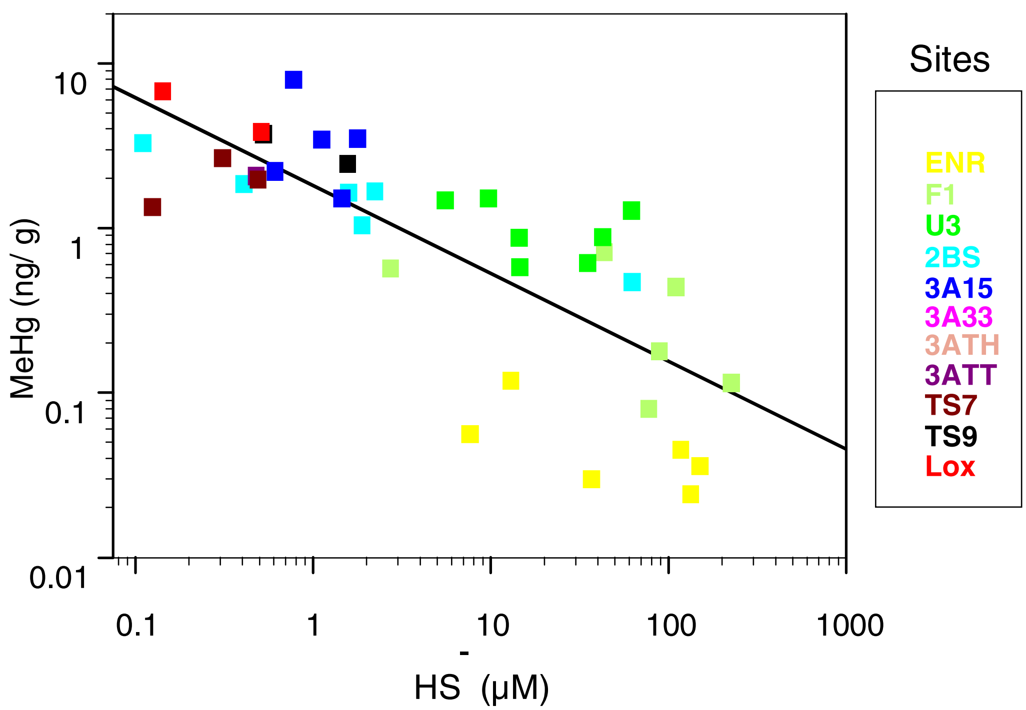


**Figure 7-14.** Sulfur cycle influences on methylmercury in Everglades peat soil: sulfide (Reproduced with permission by Cynthia Gilmour, Ph.D., ANS, St. Leonard, MD).

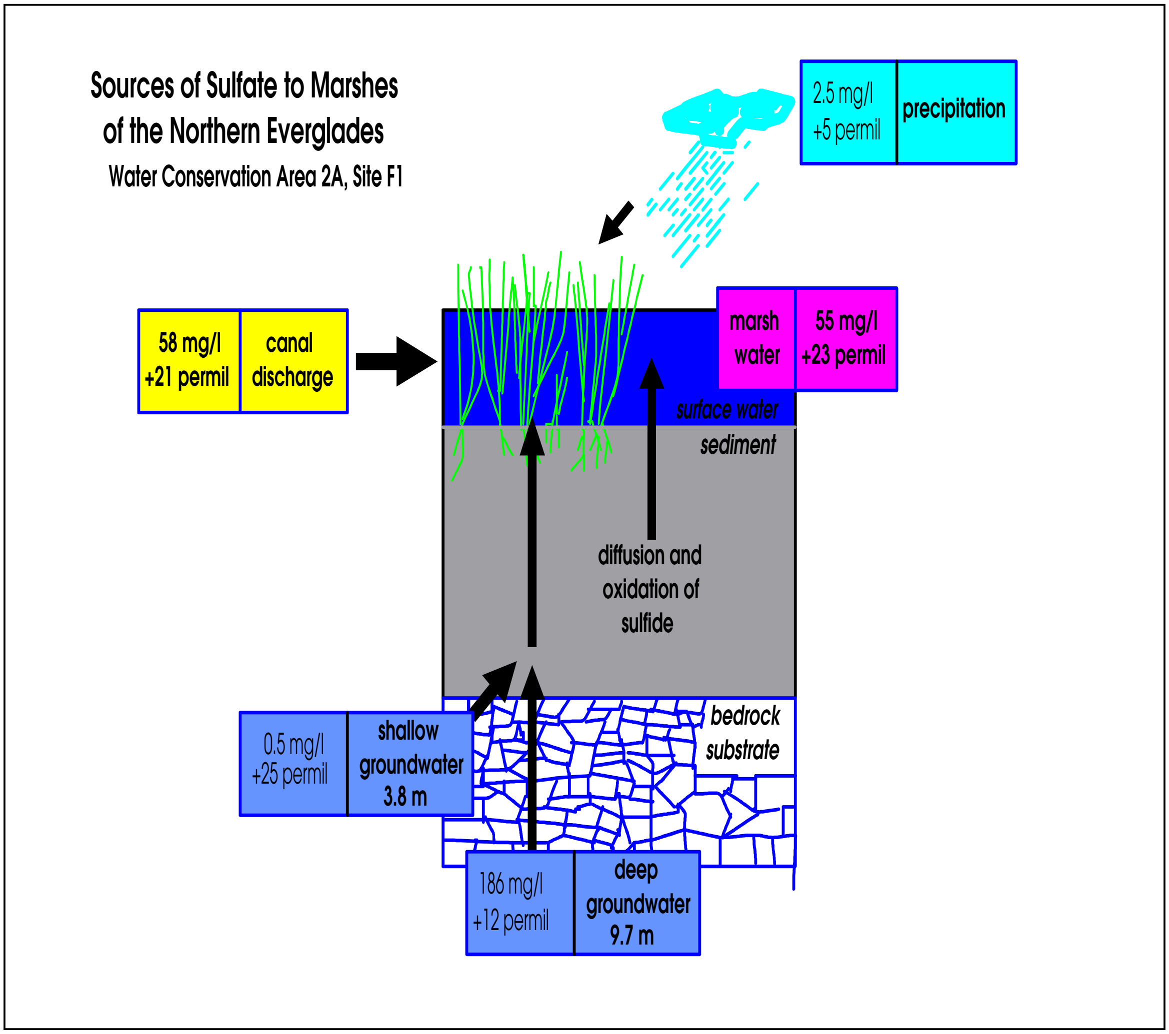


**Figure 7-15.** Source apportionment for excess sulfur in the northern Everglades (Reproduced with permission from William Orem, Ph.D., USGS-Reston, VA).

water is such that net methylmercury production is a maximum. The rate of methylation at WCA-3A-15 near the "hot spot" is one of the highest measured in any aquatic ecosystem (C. Gilmour, ANS, personal communication, 1999). However, the concentrations of total mercury, sulfate and sulfide in the soils at WCA-3A-15 and WCA-2B-S are quite similar, but the methylmercury production and bioaccumulation rates are quite different at these two sites, so other influences, like the magnitude and direction of groundwater flow, must also be taken into consideration when applying the sulfur hypothesis.

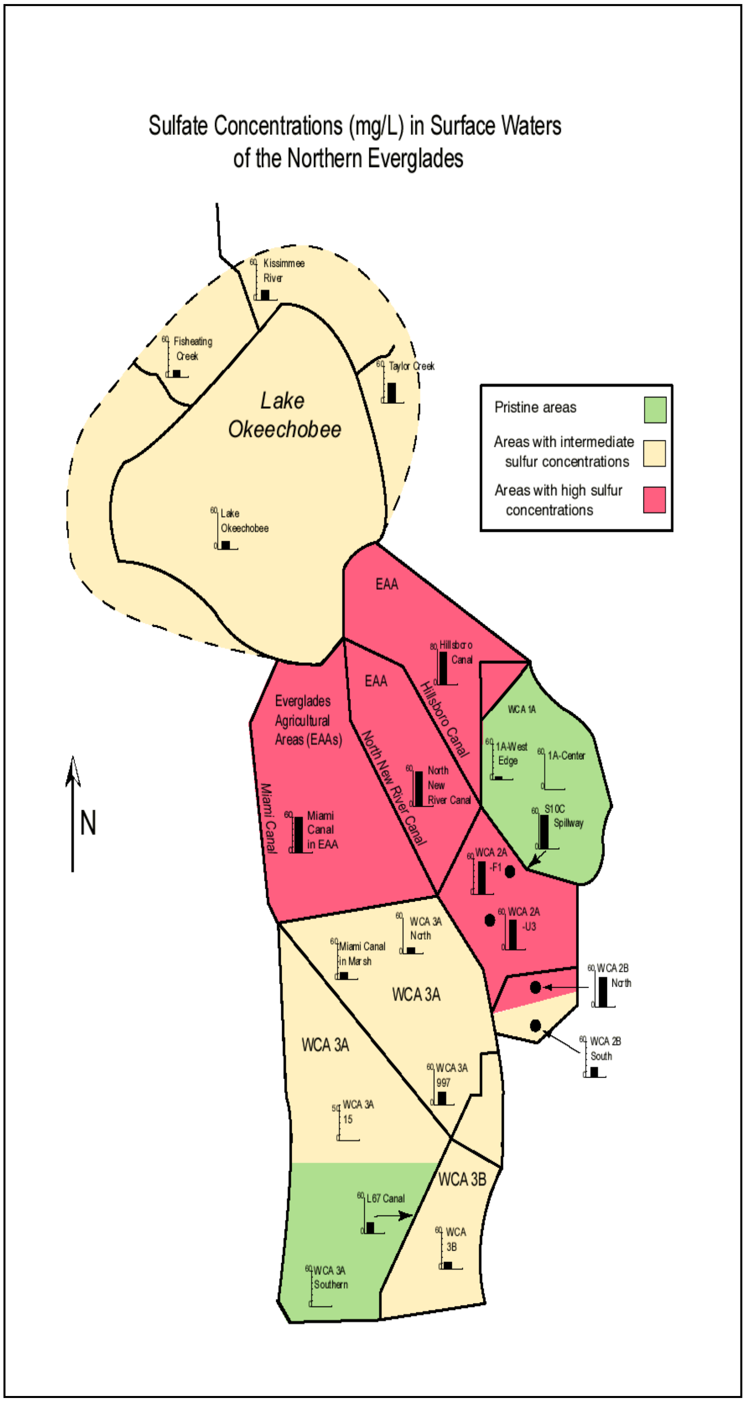


**Figure 7-16.** Spatial distribution of excess sulfate in Everglades (Reproduced with permission from William Orem, Ph.D., USGS-Reston, VA).

In addition, two alternative hypotheses for the existence of this "hot spot" must also be considered. First, the "hot spot" is in an area where water stagnates for long periods of time and the area occasionally dries out, so the combination of drying and rewetting followed by long periods of stagnation of water could foster the accumulation of methylmercury to the highest levels encountered in the Everglades, irrespective of the water or sediment chemistry occurring there. Second, the "hot spot" is downwind of Ft. Lauderdale frequently, and the air pollution transport and deposition model predicts that the maximum rate of deposition of reactive gaseous mercury on the Everglades will occur at the "hot spot" (J. Keeler, U Michigan, personal communication, 1999). If methylmercury production is being driven primarily by the new mercury supply, then the excessive deposition at the "hot spot" could explain all of the observed increase in methylmercury production and bioaccumulation there. The highest concentrations of total mercury in peat soil occur at WCA-3A-15 (Gilmour et al., 1998), which could be the product of a higher average atmospheric deposition rate and frequent drying and rewetting, together with a low peat accretion rate.

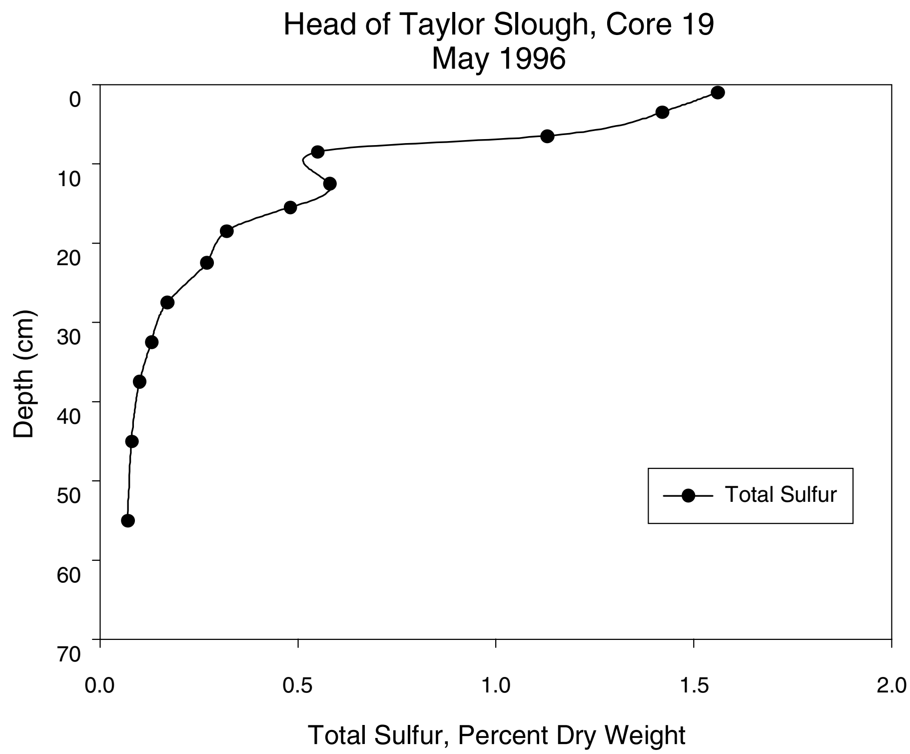


**Figure 7-17.** Vertical profile of excess sulfate accumulation in peat soil at headwaters of Taylor Slough (Reproduced with permission from William Orem, Ph.D., USGS-Reston, VA).

### The Inverse Relationship with Flow

The inorganic mercury and methylmercury in urban and agricultural stormwater runoff is transported by flowing water from District primary canals through District structures into impoundments of the northern Everglades. The inorganic mercury and methylmercury in the canals is removed slowly from the water column via sorption to settling particles and submersed plant biomass growing along the banks of or in the canals. Direct rainfall makes only a small contribution to the inorganic mercury load in the canals, because the canals have a very low surface area-to-flow volume ratio. Instead, canal chemistry, like canal transport, is dominated by surface runoff and groundwater discharge. Methylmercury is probably produced at the bottom of the canals at the sediment/water interface or in floating periphyton mats, as is the case in the marsh itself, but the required measurements have not been conducted.

When the flowing water passes through a District structure into an impounded marsh, the integrity of the plume is maintained for some distance into the marsh, depending on the differences in temperature between canal and marsh water, the types and densities of the vegetation through which the water must flow, and the submerged land features. As the more dilute water of the canals mixes with the more concentrated water in the marsh and wet and dry deposition of inorganic mercury from the air, the concentration in the flowing water increases until the distinction between the flowing canal water plume and the marsh is lost. This inverse flow dilution relationship can be quantified in WCA-2A. The concentration of total mercury at S-10C, the structure through which most EAA runoff is transported down the WCA-2A nutrient gradient, averages about 1.6 ng/L (n=7), while the average concentration at F1 is 3.1 ng/L (n=10) and that at U3 is 4.4 ng/L (n=11). The corresponding values for methylmercury are 0.13, 0.23, and 0.56 ng/L.

However, during long periods of no flow and no rainfall, the concentration at F1 can occasionally exceed that at U3, albeit only slightly. This may be due to the influence of groundwater upwelling driven by the head difference between WCA-1 and WCA-2A across the L-39 levee. A net upwelling velocity of about 0.1 cm/day for F1 has been calculated by Harvey et al., 1999. That rate decreases dramatically with distance, so that there is no measurable upwelling of groundwater at U3, even under very low head conditions during long dry periods.

## POTENTIAL DOWNSTREAM IMPACTS FROM RESTUDY

### Everglades Hydropattern Restoration

The managed hydrology of the downstream Everglades has a substantial influence on the downstream concentrations of the influential factors identified above. The influence is greatest on those factors that are least interactive with the marsh environment through transport and dilution or concentration. The magnitude of this hydrologic influence depends on the timing, routing, magnitude, and duration of surface flow, the effect of water depth of the direction and magnitude of groundwater flow, and the magnitudes of rainfall and evapotranspiration. In addition, water depth affects the penetration of sunlight (Krabbenhoft et al., 1998), the dissolved oxygen profile in water and sediments (Orem et al., 1998), and the chloride and DOM concentration profiles in water and sediments (Reddy et al., 1999), and some changes in water depth-duration are contemplated with the implementation of the interim steps of the ECP. As the changes in water depth-duration to be brought about by the ECP are minimal, the effect of the hydrologic influences on post-ECP methylmercury production and bioaccumulation must be considered of secondary importance.

Based on the ENR Project experience, all other things being equal, an increase in flow or a decrease in the HRT of the remnant Everglades impoundments should reduce both total mercury and methylmercury concentrations in water, and, where the water column is the most important source of methylmercury to the food web, in aquatic organisms and fish-eating wildlife. Some increased flow to northern WCA-3A is contemplated as a result of the construction and operation of the STAs, and this may serve to decrease the HRT and increase the water depth in many of the areas that now tend to pond or dry out for extended periods. An analysis of the potentially beneficial effects of these changes in water depth-duration must await the completion of the Restudy and a calibration and validation of the models required to conduct such an analysis with the required accuracy, precision and reliability.

### Fire Pattern Restoration

Fire is a natural Everglades phenomenon. One might speculate that fire releases inorganic mercury that would otherwise remain sequestered in refractory organic material for subsequent rapid methylation. However, fire is also likely to reduce the quantity or change the quality of organic carbon available to support microbial activity, which could reduce the rate of methylation. Dissolved organic carbon (DOC) plays an important role in mobilizing inorganic mercury for methylation,preventing sulfide precipitation (Ravichandran et al., 1998; Ravichandran, 1999) and sequestering methylmercury from demethylation and bioaccumulation. Therefore, understanding how DOC character and concentrations change after a canopy burn versus a peat burn is critical for accurately predicting the net effect of changes in the location, extent, depth, duration and frequency of recurrence of Everglades fires on the mercury cycle.

Following an extended dry period in the spring of 1999, several fires ignited in the Everglades. While most fires involved burning of emergent plant tops, in some locations where the peat had dried out extensively, the fire burned all the way to the underlying rock. These unexpected set of circumstances presented a unique opportunity to understand the influence of fire on the mercury cycle. The studies needed to fill the gaps in our scientific understanding were initiated by USGS scientists in the summer of 1999. The results of these studies will be reported in next year's Everglades Annual Report. In addition to adding to the fundamental understanding of the influence of the carbon cycle on methylmercury production and bioaccumulation, these studies are an insurance policy against inappropriately attributing positive or negative post-burn impacts on methylmercury bioaccumulation to the post-ECP influences of STAs 1W, 2, 5, which also began operation in 1999.

### Florida Bay Restoration

Florida Bay is a large (1800 square km), shallow (<2 m), estuarine system located at the southern tip of the Florida Everglades. Scientists have concluded that Florida Bay is under stress from salt water flow deprivation as a consequence of the construction of the causeway connecting Key Largo to the Florida peninsula and fresh water flow deprivation as a consequence of reduced flow from the Everglades via Taylor and Shark River Sloughs. To remedy this latter problem, among other things, the Federal Water Resources Development Act of 1996 mandates the increase of fresh water flow into Florida Bay. To meet this mandate, the Corps of Engineers is planning on increasing the fresh water flow through Taylor Slough canals into Florida Bay.

It is critical to understand how these changes in the quantity and quality of water delivery will affect the estuary. In particular, will increased delivery of Everglades water result in significant increases in mercury loading and worsen the mercury problem in Florida Bay? In 1995, the DEP, the Department of Health and Rehabilitative Services, and the Park jointly issued a health advisory recommending limited consumption of several sport fish species in Florida Bay due to elevated levels of mercury (Strom and Graves, 1995). A recent survey of mercury in fish from Florida Bay by USEPA (Kannan et al., 1998) found concentrations up to 3.9 ppm dry weight (0.78 ppm wet weight). These same authors reported high concentrations of both total mercury and methylmercury (3-7.4 ng/L and <0.002-2.3 ng/L, respectively) in filtered water samples collected from canals and creeks flowing into Florida Bay. In an ongoing study in Florida Bay, NOAA/NMFS researchers report tissue concentrations routinely exceed 0.5 ppm wet weight (criterion for limited consumption) in spotted seatrout (*Cynoscion nebulosus*), a popular recreational species (Evans and Engel, 1998). Finally, mercury also appears to be bioaccumulating in Florida Bay water birds that eat fish from the Bay of its estuaries. A study of sick or injured double-crested cormorants that subsequently died at the Florida Keys Wild Bird Center found liver-mercury concentrations of up to 250 ppm (Sepulveda et al., 1998). The maximum level from Florida Bay cormorants is more than three times the highest liver concentrations reported for Everglades great blue herons (Sundlof et al., 1994).

### Management Need

At present, little is known about the sources of mercury contamination in Florida Bay. A one-time study conducted by Skidaway Laboratory in Savannah, Georgia, suggests that Taylor Slough may make a significant contribution of total mercury and methylmercury to Eastern Florida Bay. However, it is equally plausible that inorganic mercury entering Florida Bay from the air as wet and dry deposition is sufficient to feed the internal production of enough methylmercury in Florida Bay itself to account for the magnitude and extent of the observed mercury contamination. Two years of monitoring under the Florida Atmospheric Mercury Study at Crawl Key (1994-1996) has given us sufficient information on the atmospheric deposition contribution for this scoping effort. A study of the magnitude and extent of mercury contamination of the Florida Bay food web by the National Oceanic and Atmospheric Administration suggests that top-predator fish foraging in the bays and estuaries fed by Taylor Slough may be disproportionately contaminated with mercury. However, at present no systematic study is being conducted to link Taylor Slough flow, water quality, and food organism quality to the contamination problem in Eastern Florida Bay.

Will the increased diversion of Everglades fresh water through Taylor Slough to decrease the salinity in Eastern Florida Bay while protecting the nesting grounds of the nearly extinct Cape Sable Seaside Sparrow and increase the mercury contamination problem in Eastern Florida Bay? There is insufficient information to answer this question, even at the most basic level of understanding. The inability to answer this question compromises the ability to make informed decisions about the proper management of Everglades water quantity and quality for the restoration of the sport fishery and the protection of fish-eating wildlife in Eastern Florida Bay.

### New Mercury Screening Study

To address this information gap, the District is proposing a mercury screening study to collect environmental data at three freshwater and three marine sites along the flow path of Taylor Slough into Eastern Florida Bay and a marine reference site in Western Florida Bay for comparison purposes. Water samples, three species of freshwater fish, and three species of saltwater fish will be collected quarterly, while surface sediments will be collected semi-annually. To the extent practicable, this work will be planned, coordinated, and implemented with the participation of NOAA to avoid duplication of effort, share limited resources, and generate comparable data.

## WATER SUPPLY MANAGEMENT

### Lake Okeechobee Releases

Presently, Lake Okeechobee sport fish are not contaminated with methylmercury to levels that require the posting of sport fish advisories. However, on occasion, Lake Okeechobee water may contain total mercury concentrations in excess of the concentrations in the District's canals downstream of the EAA (unpublished data, 1994). Except during flooding emergencies, Lake Okeechobee releases will be treated by the ECP before discharge to the northern Everglades. Whatever mercury-related impacts on the Everglades that might be associated with Lake Okeechobee releases will occur only as a result of discharge through the STAs. Therefore, there is no need to discuss the Lake Okeechobee impacts separately.

### New Surface Impoundments

New surface impoundments are proposed as one option for storing water in excess in the wet season for subsequent use in the dry season. Such impoundments will also serve as fisheries, which, depending on their depth and area, may also attract large populations of fish-eating (piscivorous) diving, swimming, and wading birds. These reservoirs may also experience what is referred to in the mercury literature as a "reservoir effect." The reservoir effect is summarized in **Appendix 7-5**. A more detailed discussion of the reservoir effect was presented in last year's Everglades Interim Report. In the classic reservoir effect, a post-flooding burst of inorganic mercury is released from the flooded terrestrial soil and rapidly methylated. Then the methylmercury is rapidly bioaccumulated up the food chain over a period of several years. The effect often persists for decades, especially in reservoirs with long-lived fish populations. Mercury monitoring of mosquitofish, sunfish, and largemouth bass in these reservoirs should alert South Florida restoration planners and managers to the occurrence of a reservoir effect in time to develop an appropriate adaptive management strategy to address this undesirable outcome. However, to the extent that the water in these reservoirs will be dominated by releases from Lake Okeechobee, the likelihood that a reservoir effect will manifest itself is substantially diminished, because Lake Okeechobee itself does not have a methylmercury bioaccumulation problem like that occurring in the downstream Everglades, and, as a result, has no fish consumption advisories issued for its fish.

### Aquifer Storage and Recovery (ASR)

Another water storage option is to inject excess wet season surface water into the underlying geological formations rapidly, and then withdraw it for dry season use before it can disperse into the underlying geological formations and mix with the underlying groundwater. As storing water underground virtually eliminates evapotranspiration losses that plague surface impoundments in South Florida, aquifer storage and recovery (ASR) is being given serious consideration by the hydrological engineers evaluating such option (see **Chapter 10**) . The details of the ASR project are discussed elsewhere in this report. There is some concern that the quality of ASR water will change upon withdrawal, taking on increased concentrations of some of the constituents of the underlying groundwater, including increased concentrations of calcium, chloride, sulfate, and sulfide, as well as increased alkalinity and pH, all of which are known or reasonably expected to influence methylmercury production or bioaccumulation by the mechanisms discussed in the previous section. These changes in water quality in the vicinity of the ASR releases could increase or decrease methylmercury production or bioaccumulation, although the areas of impact might be quite small in proportion to the already impacted areas of the Everglades. Modeling of the potential mercury-related impacts of ASR releases will be supplemented with subsequent monitoring of fish near the discharges to determine whether this concern is well-founded.

## WHAT TOOLS ARE REQUIRED TO UNDERSTAND AND SOLVE THE EVERGLADES MERCURY PROBLEM?

The new tools for collecting and analyzing various mercury species in environmental media are discussed in the next section that answers the question: What is the status of District and DEP efforts to understand and solve the Everglades mercury problem? The tools required to link sources to environmental impacts are discussed in this section. These tools are air and water quality mathematical models. Mathematical models will be required to predict the effect of local air source reductions on atmospheric deposition to the Everglades and to predict the effect of that load reduction on the production and bioacccumulation of methylmercury in the Everglades ecosystem. The former modeling will be conducted by University of Michigan researchers under contract to USEPA Region 4 and DEP. An existing model of air emissions plume transport, transformation, and deposition (e.g., HYSPLIT) will be used for this purpose and calibrated with local source emissions data and near- and far-field wet and dry deposition data (J. Keeler, U Michigan, personal communication, 1999). The latter modeling will be conducted by Tetra Tech, Inc., under contract to USEPA's Office of Research and Development, DEP, and the District. The Everglades Mercury Cycling Model 2 (EMCM-2) will build on the advances incorporated in EMCM-1, which was developed, adapted, and applied to Everglades problem-solving by USEPA's ORD in Athens, Georgia (Ambrose and Araujo, 1998).

### AIR TRANSPORT, TRANSFORMATION, AND DEPOSITION MODELING

Off-the-shelf models are being used as is for simulating mercury transport, transformation, and deposition from local air emissions sources. The models are being calibrated with data obtained in the South Florida Mercury Atmospheric Study (SOFAMS) conducted in the late summer of 1995 and the more recent FEDDS, which began in February-March 1999.

Precipitation samples were collected at a site in Davie, Florida, on a rainfall event basis for one year from June 22, 1995, to June 21, 1996. The samples were analyzed for a variety of common ion and toxic metals, including total mercury. The data were then used to test the hypothesis that local sources in Ft. Lauderdale and environs are the most significant influence on mercury deposition in precipitation at the Davie site. To achieve this objective, a hybrid modeling approach was used. First, the Hybrid Single Particle Lagrangian Integrated Trajectories (HYSPLIT) model was used to determine the pathway followed by the air parcels arriving at the Davie site over the previous day, so-called daily back trajectories. This was done for each day of the study. Second, the daily back trajectories were grouped into 15 distinct atmospheric transport regimes using a statistical model of similarity. Third, the model RAMS was used to generate the three-dimensional wind and heat fields for a representative day selected from each of the 15 distinct groups. Fourth, the NOAA HYSPLIT model, initialized with the wind and heat fields for a typical day from each of the 15 distinct atmospheric regimens, was used to estimate the transport and deposition of mercury at the Davie site using mercury emissions estimates from the USEPA inventory for the source categories in the Ft. Lauderdale area.

Each of the 15 model runs was then multiplied by the frequency with which it occurred in the study year to calculate the annual weighted average deposition of mercury to the Davie site. The results indicate that more than 90 percent of the deposition at the Davie site originates with local sources. However, because the Davie site is well east of the Everglades, it is not yet clear whether the set of models calibrated to the Davie site can accurately predict the mercury deposition rate 100 km to the west over the Everglades. Until the Ft. Lauderdale source-deposition modeling results are reconciled with the earlier FAMS data, the results of these modeling exercises must be considered preliminary at best.

## WATER TRANSPORT, TRANSFORMATION, AND BIOACCUMULATION MODELING

If one uses a multivariate regression analysis to pick out the two or three variables that have the greatest influence on methylmercury bioaccumulation in mosquitofish along the WCA-2A nutrient gradient, one might select alkalinity, DOC or calcium or DOC and calcium for this purpose (See Appendix 7-3 in Chapter 7 of last year's Everglades Interim Report (Rumbold and Fink, 1999). If the District's two-variable regression relationship based on water column DOC and calcium is then used as a predictive tool, it could be concluded that the STAs will have no significant effect on methylmercury bioaccumulation in mosquitofish, because the STAs do not remove DOC or calcium and post-STA concentrations of DOC and calcium will not change substantially in the already impacted areas as they recover from the effects of excess phosphorus. This is one example of the misuse of a regression relationship to predict post-ECP methylmercury exposures and risks. This approach has no scientific merit because it ignores the role of phosphorus in influencing inorganic mercury and methylmercury sorption to settling plant biomass and subsequent dilution in the undecomposed plant biomass that forms peat soil. It also ignores the influence of methylmercury production in the eutrophic periphyton mat and the influence of peat pore water sulfide on methylmercury production.

At the other extreme, one could use the Sugar Cane Growers Cooperative's one-variable regression relationship based on water column phosphorus (PTI, 1995a,b; PTI, 1997; Exponent, 1998) to predict that the STAs will cause the methylmercury concentrations in mosquitofish to increase 660 percent as water column total phosphorus concentrations decline from about 50 ppb to 10 ppb in the already impacted areas of the northern Everglades.

This prediction also has no scientific merit, because it ignores the role of DOC and hardness in influencing sorption and uptake by microscopic plants and animals at the base of the food chain, which, in turn, determine the bioaccumulation of methylmercury at each successive trophic level in the food chain. It also ignores the influence of methylmercury production in the eutrophic periphyton mat and the influence of peat pore water sulfide on methylmercury production.

In fact, neither statistical model has scientific merit or engineering utility, because both leave out or misrepresent key relationships between water chemistry and methylmercury production or bioaccumulation, as well as key process influenced by hydrology and meteorology. Sufficiently reliable predictions of the influence of the operation of the STAs on the downstream production and bioaccumulation of methylmercury can only come from a model that takes into account in a self-consistent, mechanistically realistic way the positive and negative influences of the above identified constituents and factors on the downstream mercury cycle. The second generation of such a model is now under development. A summary of the key features of this model and the results of its first-generation application to the problem of predicting post-STA mercury risks to wading birds is taken up in the following subsection.

### Model Development

EMCM-1 is a mercury transport, cycling, and bioaccumulation model that has evolved from earlier models used extensively by USEPA to guide policy-level decision-making, source control and site cleanup. The model is a modification of the toxic chemical module of WASP5, TOX15. WASP5 is the general water quality model adopted by USEPA for many policy analysis and regulatory applications. EMCM-1 incorporates the main structural features of the Mercury Cycling Model developed by TetraTech for the Electric Power Research Institute, except that the chemical complexation and food web routines are replaced by simpler partition coefficients and bioaccumulation factors that are calibrated to Everglades data. To this basic framework has been added features that allow the user to quantify the effect of changing total phosphorus in the water column on the standing crop densities, production rates and decomposition rates of attached algae communities (periphyton), emergent macrophytes (e.g., sawgrass and cattail) and floating macrophytes (e.g., water hyacinth and water lettuce). These densities and rates are quantified using simple regression relationships derived from earlier data collected by District scientists in WCA-2A along the same nutrient gradient (e.g., Swift and Nicholas, 1987; Davis, 1989; 1991). Model unknowns (i.e., the fractions of refractory organic and inorganic components of cattail, sawgrass, floating macrophytes, and periphyton) are obtained via calibration to the composition of the peat soil at the simulated site or segment.

The average annual fraction of the area covered by macrophyte communities has been obtained from aerial photography conducted by District staff, while the annual average fraction of area covered by periphyton has been obtained from the best professional judgment of District scientists that routinely visit these sites. The relative affinities of inorganic mercury and methylmercury for the dissolved, suspended solids, and DOC phases is assumed to follow a simple linear three-phase partitioning model, with the values of the partition coefficients coming from site-specific Everglades studies. The affinity of these species for macrophyte leaves has been adjusted to fit observations from other the ENR Project and elsewhere. The rates at which the various biogeochemical processes occur are modeled by multiplying the concentration of the mercury species involved by an appropriate rate coefficient. The magnitudes of the rate coefficients have been calculated from published site-specific Everglades research data. In this version of the model, bioaccumulation in mosquitofish is calculated from site-specific bioaccumulation factors obtained from calculations using field data.

Further refinements that had been proposed for the Everglades Mercury Cycling Model-1 include linking the water quality model to a food chain bioaccumulation model (FGETS) that will simulate methylmercury bioacumulation via water and food in a representative aquatic species at each of three trophic (feeding) levels in the Everglades food chain.

### Water Quality Model Applications: Post-ECP Impacts

The areas in the northern Everglades already impacted by total phosphorus in EAA runoff are likely to undergo the most significant changes in water and sediment quality after the ECP is completed and the operation of the majority of the STAs has begun. As with the ENR Project that preceded them, the STAs are likely to remove more than 75 percent of the total phosphorus, 50 percent to 75 percent of the total mercury, and less than 10 percent of the sulfate in EAA runoff and Lake Okeechobee releases. While the sulfur cycle fed by sulfate in EAA runoff is probably the strongest determinant of downstream methylmercury production (Gilmour et al., 1998b), one might expect that the reduction in water column total phosphorus and total mercury will also have an effect on downstream methylmercury production and/or bioaccumulation. This effect should be maximized at the sites nearest the District structures. This subsection summarizes the results of the modeling analysis in last year's Everglades Interim Report, recognizing that no substantial changes in model process representations, coefficients, or starting conditions are required based on what has been learned in the SFMSP since last year.

The objective of this modeling exercise was to address the potential benefits and detriments of a simultaneous 75 percent reduction in total phosphorus and 50 percent reduction in total mercury on the already impacted areas immediately downstream of District structures. For this purpose, the WCA-2A nutrient gradient was selected. There are six study sites along this nutrient gradient, ranging from the most impacted (eutrophic) site at F1, about 1.8 km down gradient from the discharge structure at S-10C, to U3, the least impacted (oligotrophic) site at 10.8 km down gradient. To simulate post-ECP downstream total mercury and methylmercury concentrations in water, sediment, plants, and fish, a 10-km wide by 7.5-km long box was constructed over the study sites. The 7.5-km length was chosen as the demarcation of the point where annual average water column concentrations of total phosphorus now fall below 10 ppb. To conduct the required simulations, the EMCM-1 model was adopted by USEPA Office of Research and Development in Athens, GA.

The model was initialized with the rate coefficients (Gilmour et al., 1998; Krabbenhoft et al., 1998; Marvin-DiPasquale and Oremland, 1998), partition coefficients (Hurley et al., 1998; Gilmour et al., 1998; Aiken and Reddy, 1997), and bioaccumulation factors (Cleckner et al., 1998; USEPA, 1998) observed at the most oligotrophic site along the WCA-2A nutrient gradient, U3, where annual average total phosphorus concentrations are already about 8 ppb (District, unpublished data, 1999). The model was next calibrated to the observed concentrations in water, sediment and mosquitofish at U3 and then run with a constant total phosphorus concentration of 50 ppb for 50 years to ensure that water and sediment concentrations reached a steady state. With a reduction in water column total phosphorus from 50 ppb to 10 ppb but without the 50 percent mercury load reduction, the model predicted an increase in mosquitofish mercury of about 55 percent. This is more than an order of magnitude lower than the 660 percent predicted by the one-variable (water column TP) exponential regression model (PTI, 1995a,b; PTI, 1997; Exponent, 1998). With a reduction in water column total phosphorus from 50 ppb to 10 ppb and with the 50 percent reduction in the inorganic mercury load, the model predicted an increase in mosquitofish mercury of 42 percent. This is only about 6 percent of the increase predicted by Exponent's one-variable regression model. From this analysis, it can be concluded that the PTI/Exponent model likely overestimates the detrimental effects of a reduction in biodilution and cannot address the positive effects of the anticipated post-ECP reduction in the total mercury load.

If a series of smaller boxes is used to model these post-ECP effects, it is expected that the benefit from post-ECP mercury load reduction at F1 is likely to be even greater than the average benefit distributed over the length of the 7.5 km box. This hypothesis will be tested by Tetra Tech while under contract to DEP with successive refinements of EMCM-2 over the next several years. The preliminary results of this reassessment will be included in next year's Everglades Consolidated Report.

The Everglades Mercury Cycling Model-1 model has acknowledged limitations, e.g., it cannot model the influence of peat pore water sulfide in EAA runoff on methylmercury production. Nevertheless, it is able to represent in a self-consistent way the influences of water column total phosphorus on plant densities, production rates, and decomposition rates, peat soil production, and inorganic mercury and methylmercury removal rates from the water column via sorption to settling biomass. This accounts for one of the three key mechanisms believed to cause or contribute to the inverse relationship. The model also uses the observed mosquitofish bioaccumulation factor at U3, where annual average water column concentrations of total phosphorus are already less than 10 ppb, to calculate the concentration of methylmercury in mosquitofish from the model-estimated concentration of methylmercury in water. This bioaccumulation factor takes into account any changes in species composition and feeding habits and any loss of methylmercury biodilution due to a reduction in the densities and turnover rates of plant species and the densities and growth rates of animal species at each step in the food chain. This accounts for the second of the three key mechanisms believed to cause or contribute to the inverse relationship. Finally, by using the methylation and demethylation rates measured at U3, this accounts for the influence of the dissolved oxygen, sulfate, and sulfide concentration profiles in water and peat soil on the location, activity, and inorganic mercury uptake and methylation efficiencies of sulfate-reducing bacteria and the methylmercury uptake and demethylation efficiencies of the demethylating bacteria, either directly or via the sulfur cycle.

Thus, the model is believed to provide reasonable first-order predictions of the post-ECP methylmercury concentrations in fish in WCA-2A immediately downstream of the S-10 structures in response to a simultaneous reduction in total phosphorus and total mercury concentrations and loads. These first-order predictions supplement other, non-modeling evidence to further support the conclusion that it is <u>highly unlikely</u> that the ECP will cause or contribute to an environmentally significant increase in use impairment or mercury risks to fish-eating wildlife.

The model cannot yet be used to determine if there would be a net downstream benefit or detriment with respect to methylmercury production and bioaccumulation if the use of sulfur on EAA soils were reduced or curtailed. The upgrades to the model will include better linkages to a EAA mercury runoff model (Tsiros and Ambrose, 1999) and between the sulfur cycle and the mercury cycle to address the EAA sulfur management question over the next few years.

### Water Quality Model Applications: Restudy Alternatives

There have been no new applications of EMCM-1 to the prediction of post-Restudy mercury impacts this reporting year. The potential mercury impacts of proposed Restudy restoration projects, including reservoir creation, ASR, and the C-111 Basin Project, are discussed in qualitative terms in the subsection that answers the question, How will Everglades restoration affect mercury risks?

## BIOACCUMULATION MODELING

Craig Barber of USEPA's Office of Research and Development in Athens, Georgia, has completed preliminary model runs of a BASS, a bioenergetics-based food web model, adapted to the conditions and food web structure of the Everglades. The model is able to explain the large differences in mosquitofish bioaccumulation of methylmercury observed between sites in terms of differences in ambient methylmercury concentrations that are amplified by differences in feeding preferences (C. Barber, USEPA/ORD-Athens, personal communication, 1999).

The bioenergetics-based bioaccumulation model incorporated into the modified Everglades Mercury Cycling Model-2 will be able to reproduce many of the features of BASS and its key results.

# WHAT IS THE STATUS OF DISTRICT AND DEP EFFORTS TO UNDERSTAND AND SOLVE THE EVERGLADES MERCURY PROBLEM?

## SUMMARY

The DEP and the District continue to foster the development of new sample collection methods for reactive gaseous mercury and near real-time analysis of reactive gaseous mercury and dissolved gaseous mercury, while USGS continues to advance the understanding of the sources of excess sulfur in the northern Everglades, the cycling of mercury and the factors that influence the mercury cycle, and the structure of the Everglades food web and the migration patterns of top-predator fish using natural and enriched stable isotopes. The District and DEP continue their leadership roles in the SFMSP. DEP will be sponsoring the Mercury Intercomparison Program for ultra-trace total mercury and methylmercury analytical methods. In 1998-1999, the District and DEP funded research on the factors influencing methylmercury production. Next year, the District and USEPA will continue to fund this and related studies. In 1998-1999, DEP and the District continued the model development project begun by USEPA to ensure that the second generation Everglades Mercury Cycling Model incorporates the influences of phosphorus and sulfur on the mercury cycle, and this work will continue for two more years.

DEP an USEPA will continue support for air source emission, transport, and deposition monitoring and modeling. Pursuant to Act requirements, DEP has determined that the existing Class III numerical Water Quality Standard for total mercury is inadequate to protect the use of the resource as a sport fishery. A new analysis in this report suggests that the existing human health action level of 0.5 mg/Kg may not be fully protective of Florida panthers that feed on raccoons, even occasionally. The District will continue to press for follow-up studies of the uptake, distribution, and elimination of methylmercury in the alligator, the wood stork, the otter, and Florida panther or appropriate surrogate species.

The science and regulatory initiatives required to meet state mandates in the Everglades Forever Act and federal mandates in the Clean Water Act are summarized in the proposed Everglades Mercury Action Strategy (E-MAS), which is reproduced in its entirety in Appendix 7-1. Only a few of the breakthrough studies that were conducted in 1999 will be summarized here. The results of key findings from Phase 1 studies are summarized in the previous section answering the key questions.

## AIR STUDIES

An instrument developed under contract to USEPA and DEP for collecting reactive gaseous mercury (RGM) in air has been tested at the eastern edge of the Florida Everglades and found accurate, precise, and reliable in its measurements (R. Stevens, USEPA-retired, personal communication, 1999). Tekran ultra-trace mercury vapor analyzers owned by DEP and the District have been modified for RGM analysis and loaned to the University of Miami for research into the gas-phase chemistry that explains the night and day transformations of elemental mercury, which is not readily removed by rainfall, into RGM, which is readily removed by rainfall. The results of this study will improve the accuracy of the model of air emissions plume transport and deposition over the Everglades.

To reduce the uncertainty associated with the quantification of the global background contribution to Everglades atmospheric deposition, a research plane owned by the National Oceanic and Atmospheric Administration has been chartered by DEP and USEPA to fly the new RGM analyzer into the upper troposphere for the to collect RGM at several different altitudes. If concentrations of RGM are relatively high and increase with altitude, this will support the hypothesis that RGM is being generated continuously by the strong sunlight in the upper atmosphere to produce a large pool that can be scavenged by the tall thunderheads that develop over South Florida during the wet season without a significant decrease in inorganic mercury concentrations in rain as the thunderstorm proceeds. Together, these results may explain why summer wet deposition concentrations and loads are more than double those in the dry season, while local air emissions sources are relatively constant year around (W. Landing, FSU, personal communication, 1999).

The Florida Emissions Dry Deposition Study (FEDDS) is being conducted by Principal Investigators from the University of Michigan, USEPA's Office of Research and Development in Research Triangle Park, and Oak Ridge National Laboratory. The objectives of this study are to quantify the dry deposition of RGM and particles directly to water surfaces and to dry and wet plant surfaces with subsequent washoff to the adjacent water surface, taking into account wind direction, speed, and duration and time of day. Studies to prove the concept and validate the sampling equipment were conducted at the L-67A site at the eastern edge of the Everglades in February-March 1999. The preliminary results of this first campaign suggest that RGM deposition in the late winter is about equal to the rainfall deposition rate for the same period. If these same proportions hold for the wet season, this would roughly double the 22 ug/m$^2$-yr average deposition rate for the Everglades calculated from the 1993-1996 Florida Atmospheric Mercury Study (FAMS), which focused on the contribution of rainfall and particle deposition only. The FEDDS project data will also be used to calibrate and validate an air transport, transformation, and deposition model to test the hypothesis that local sources can account for virtually all of the dry and wet deposition on the Everglades, including the higher deposition rates in summer wet season versus the winter dry season.

The FEDDS project is being co-funded by DEP, USEPA Region 4, and USEPA's Office of Research and Development. The District is supporting this effort by providing permanent platforms and portable generators.

## WATER STUDIES

Lindberg et al., (1998) developed a new method for near real-time analysis of elemental mercury in water. DEP and USGS-Madison have both purchased the new automated analyzer for total mercury in water marketed by Tekran, LTD. The Tekran has reduced DEP's method detection limit from 0.5 parts per trillion to 0.2 parts per trillion, while increasing the precision of its results, especially in the low concentration range. The lower MDL was needed for monitoring sites like the ENR Project, where outflow concentrations were consistently less than 0.5 parts per trillion. Minor modifications of the Tekran instrument by

USGS-Madison have been reported to increase its precision almost 10-fold (D. Krabbenhoft, USGS-Madison, personal communication, 1999).

Following a rather extended dry season probably brought on by La Nina, a rather extensive series of fires occurred in the Everglades that burned plant canopies and, in some locations, also burned some of the surficial peat deposits all the way down to sand or marl. Such burning of plants and peat may have liberated inorganic mercury for methylation at a rate heretofore not encountered in the Everglades during Phase 1 of the SFMSP. In addition, the character of the dissolved organic matter present in peat pore water or the overlying water column may have changed at and downstream of these burn sites, which could be expected to change the transport, disposition, and perhaps even the methylation rate of inorganic mercury or the bioaccumulation factors of methylmercury.

To ensure that such post-burn changes in methylmercury production and bioaccumulation are not attributed to post-ECP changes in water quantity or quality, an intensive study at 13 interior marsh sites was conducted by the USGS-Madison in July 1999. A follow-up study is planned for the late fall. Along with the routine collection of water, vegetation, and fish, a newly acquired stable mercury isotope capability for tracing the routes and quantifying the rates of methylation and demethylation processes was applied for the first time to sediment cores collected from burned and unburned sites. The results of these studies will be summarized in next year's Everglades Annual Report. The July 1999 study was funded by the District with 40 percent matching funds from the USGS Regional Office. The fall follow-up study will be funded at 100 percent by USGS-Madison. In both campaigns the District provided airboat and helicopter access to study sites. In the interim, the District has proposed to collect water, sediment, and mosquitofish for USGS at 7 of the 13 sites in August, September, and October 1999, resources permitting.

To identify, characterize and quantify the physical, chemical, and biological influences on the fraction of inorganic mercury in soil for available for methylation, two lines of research will be pursued. The first will involve a functional definition of bioavailability. First, the inorganic mercury in hydrated peat soil will be sequentially extracted using an appropriate range of concentrations of hydrogen ion, carbonate ion, dissolved organic carbon, short-chain fatty acids, calcium ion, iron ion, and sodium sulfide ion solutions under anoxic conditions. Second, the gross methylation rate will be quantified in the soil after each sequential extraction by incubating the cores for a period of 28 days. Correlation analyses can then be conducted to quantify the relationships between methylmercury bioaccumulation in periphyton and fish and the normalized inorganic mercury concentration in the soil. The methylation rate can also be normalized to the inorganic mercury fractions that are bioavailable for methylation. A similar experiment can be conducted for methylmercury to define its bioavailable fractions for demethylation. The second line of research will involve the addition of stable isotopes to microcosms and mesocosms to qualify the routes and quantify the rates of transport, sorption, chemical reaction, biouptake and microbiological transformation. The results of the two approaches will be compared to validate the less expensive functional approach with the more expensive but scientifically rigorous isotope tracer approach.

To measure the influences of various water chemistry variables and temperature on methylmercury production and decomposition, Everglades sediment cultures will be spiked with radiolabelled inorganic 203-Hg (II) and 14-C methylmercury and incubated for at least 28 days to measure gross methylmercury production and gross methylmercury decomposition, from which net methylmercury production can be calculated. The concentrations of appropriate water constituents will be varied over three monotonically increasing concentrations at three monotonically increasing temperatures with replication. The sensitivities of gross methylation and demethylation and net methylation processes to changes in water chemistry and temperature will be reported. In addition, the studies of Gilmour and co-workers at the Academy of Natural Sciences and Hurley and co-workers at the University of Wisconsin-Madison will continue in FY 2000 under a 3-year USEPA STAR Grant. Recently, the USGS-Madison has acquired a quadrupole mass spectrometer capable of quantifying the different isotopes of mercury at environmentally relevant concentrations. It will be used to conduct natural isotope spiking experiments to probe the underlying chemistry and microbiology of the influence of the sulfur cycle on the mercury cycle. Such experiments can be superimposed on those described above to further resolve the routes and rates by which the various processes of interest occur.

The District is proposing to expand its mercury screening studies into Taylor Slough and Florida Bay to quantify the influence of Taylor Slough mercury concentrations and loads on Florida Bay water quality.

## BIOACCUMULATION AND FOOD WEB STUDIES

Studies by Ted Lange and co-workers of the FFWCC indicate that mosquitofish make up only a small fraction of the stomach content of largemouth bass at all canal and interior marsh study sites (Lange et al., 1999), but this may not be the case during extended dry season conditions, when some largemouth bass are trapped in deep pools in the interior marsh and are forced to feed on what is present there (W. Loftus, USGS, personal communication, 1999). These studies also indicate that a disproportionate fraction of their stomach contents is crayfish at some interior marsh sites, including WCA-3A-15 (T. Lange, FFWCC, personal communication, 1999). To date, however, the crayfish has not been targeted for collection at these sites. To fill this data gap, the District will distribute crayfish traps at these sites for collection by FFWCC staff during the fall permit compliance collection of interior marsh fish. These traps were used successfully at the ENR Project.

The DEP and the District co-funded the FFWCC feeding preference studies through 1999. DEP will continue to support this work, while the District will support the permit compliance monitoring at the twelve interior marsh sites.

Carol Kendall and co-workers of the USGS-Menlo Park are using isotopes of carbon, nitrogen, and sulfur to reconstruct the average feeding habits of mosquitofish and largemouth bass over the entire Everglades canal and marsh system. Isotopes are transferred from prey to predator at different rates, so there is a shift in the abundances of the isotopes in predators relative to their prey. These shifts are then used to reconstruct typical feeding patterns. Applying this approach to subsamples of largemouth bass collected by FFWCC throughout the Everglades canals and marshes, Dr. Kendall has concluded that bass that feed primarily in the canals have isotope abundance patterns that are distinct from those feeding primarily in the marsh. This indicates very different food webs in the canals and marshes, but this also makes it possible to determine the fraction of the time a largemouth-bass population spent feeding in the marsh and the adjacent canals. This latter information reinforces the results of radiotelemetry studies of largemouth-bass movement initiated on a small scale by the FFWCC. The ability to determine spatial differences in food web structure and the range over which largemouth bass feed within that variable environment is necessary for quantifying the influence of water levels on bass mobility and in properly reconstructing the average diet and the average environment of the populations being sampled.

Hundreds of mosquitofish collected by USEPA Region 4 throughout the Everglades in the period 1994-1996 have also been analyzed for their isotope abundance shifts to map distinctly different food web regions. Having analyzed mosquitofish from populations whose gut contents have been studied by others (P. Garrison, WDNR-Madison, personal communication, 1999), Dr. Kendall has concluded that while periphyton makes up as much as 40 percent of the gut contents of the mosquitofish, the carbon and nitrogen isotope shifts are inconsistent with periphyton being a substantial food source to mosquitofish. Whether the mosquitofish is able to absorb methylmercury from the periphyton that is not absorbed for its food value cannot be determined from this study, however, and needs to be a priority for SFMSP Phase 2 research. The District will also be splitting samples of great egret eggs collected at colonies in WCA-3A with Dr. Kendall for isotope analysis to determine the average diet of the females that laid these eggs and reconstruct a typical food web for these highly exposed birds. This is the first time that a study of this kind has been conducted in the Everglades. This work is being supported by the USGS.

The District is proposing to expand its mercury screening studies into Taylor Slough and Florida Bay to quantify the influence of Taylor Slough mercury concentrations and loads on Florida Bay fish. This work will be coordinated with a related set of studies being conducted by NOAA.

## PHARMACOKINETICS AND TOXICITY STUDIES

For the Everglades otter, mink and Florida panther, there is significant uncertainty regarding the efficiency with which methylmercury is absorbed across the gut, its subsequent disposition amongst the organs and tissues, its decomposition routes and rates to inorganic mercury, and the excretion rates of inorganic mercury and methylmercury via hair, kidney, liver and offspring. These studies can be organized under the category of pharmacokinetics studies. Using pharmacokinetics data, it is possible to relate the toxic concentrations in the organs or tissues of a test species to an untested species more accurately than by using a simple body weight- or surface area-equivalence model. It is also possible to reconstruct an exposure history from methylmercury and inorganic mercury residue levels in the body. This makes it possible to test various assumptions about contact frequencies and feeding preferences that can otherwise only be obtained by expensive, multi-year studies involving animal tracking and field observation.

The required pharmacokinetics studies can be conducted in phases. In the first phase of the study, otter removed from the wild and farm-raised mink would be fed clean ration and monitored for the decrease in blood, fur, lipid, urine, and feces methylmercury and inorganic mercury concentrations over time. In the second phase of the study, the otter and mink would be dosed with dually radiolabelled methylmercury (203-Hg and C-14) in ration to define the methylmercury uptake efficiency across the gut, the disposition of methylmercury and inorganic mercury in the organs and tissues, and their concentrations in excreta without requiring the sacrifice of the animal. The maximum methylmercury body burden that is accumulated during the second phase of the study would not exceed that in the animal at the time it was withdrawn from the wild. In the third phase of the study, clean ration would be substituted for the dosed ration and the depuration from individual organs would be determined from the localized loss of signature radioactivities. The data would be used to construct a pharmacokinetics model of the otter and the mink. If determined to be necessary, sacrifice of a limited number of animals would allow validation of the nondestructive methods and the development of appropriate correction factors. The corrected mammalian pharmacokinetics model could then be applied to the otter and mink data to calculate a target organ-based mink NOAEL and an equivalent otter NOAEL.

The decision whether to conduct the pharmacokinetics studies outlined above in Phase 2 of the SFMSP has not yet been made.

## ASSESSMENT STUDIES

USEPA Region 4 has completed an analysis of the data from its South Florida spatial characterization study, called REMAP, looking at the combined effects of water depth, phosphorus, and mercury on overall the health of the Everglades. For this purpose the Everglades was divided into three zones: above Alligator Alley, between Alligator Alley and Tamiami Trail, and below Tamiami Trail. The results will be presented at the Annual Mercury Meeting of the SFMSP in Atlanta, GA, in June of 1999. The District will present the results of its ecological risk assessment (ERA) of methylmercury toxicity to wading birds feeding in post-ECP impacted areas of the Everglades at that same meeting. **Appendix 7-4** contains an evaluation of the adequacy of the fish consumption action level of 0.5 mg/Kg to protect the Florida panther feeding on raccoons.

## PLANNING AND MANAGEMENT

**Appendix 7-1** contains the District's Everglades Mercury Action Strategy (E-MAS), which is intended to guide the development of plans, timetables, and budgets over the next five years and bring the extremely successful SFMSP to a successful close. The E-MAS will be a primary topic of discussion at the upcoming Management Committee Meeting of the SFMSP in the late summer of 1999.

In summary, the E-MAS will guide the following actions:

- Adoption of a new water quality standard to protect human health following USEPA's lead.
- Development of a new water quality standard to protect fish-eating wildlife.
- Development of a Site-Specific Alternative Criteria for the Everglades based on the new USEPA and Florida WQC.
- Quantification of abatable loads from local air emissions sources.
- Quantification of non-abatable loads from recycling of inorganic mercury in the sediment and atmospheric deposition from the global reservoir.
- Quantification of the methylmercury assimilative capacity in the form of a Total Maximum Daily Load (TMDL) of the Everglades with an appropriate margin of safety using process data and the Everglades Mercury Cycling Model-2.
- Development of a waste load allocation (WLA) for air, water, and groundwater pathways and local sources.
- Development of a permit conditions to control abatable air emissions sources.
- Take other appropriate actions to reduce the propensity of the Everglades to generate and bioaccumulate methylmercury.

In September 1999, the District and DEP will participate in a meeting of the Management Committee of the SFMSP with the other major participants in the SFMSP. The main topic for discussion is the so-called "end-game" strategy for:

- Promulgating a revised total mercury water quality standard fully protective of human health and fish-eating wildlife and their predators
- Developing, initializing, and calibrating a model that predicts methylmercury concentrations in water, sediment, fish, and birds from the inorganic mercury loading rate
- Regulating sources under post-ECP conditions of water quantity and quality to attain and maintain the revised total mercury water quality standard in the Everglades.

To support the revision of the total mercury water quality standard for the protection of wading birds, in October 1999, the District and DEP will co-sponsor a workshop to achieve consensus on our understanding of the methylmercury exposures and risks to Everglades wading birds and to finalize the SFMSP Phase 2 study plan for quantifying methylmercury toxicity, exposures, and individual and population-level risks to wading birds.

## QUALITY ASSURANCE

Each of the agencies and contractors participating in the SFMSP is required to have a USEPA-approved or equivalent Comprehensive Quality Assurance Plan for its analytical laboratory and a Quality Assurance Project Plan (QAPP) or equivalent for each of its projects that require field sampling. In addition, the DEP and then the District conducted intercomparison studies of the ultra-trace mercury laboratories participating in the SFMSP. Excellent agreement was achieved among laboratories for both total mercury and methylmercury in a composite fish sample from the Everglades. As expected, water results were more variable (Rawlik, 1999).

## REGULATION

USEPA is sponsoring two projects to test the legal and technical elements of the new regulatory guidance for developing and implementing the watershed total maximum daily load (TMDL) requirement contained in Section 303(d)(1)(C) of the Clean Water Act for air emissions sources of the problem pollutants (BNA, 1999b). Mercury was chosen as the test pollutant. This will require the development of a relationship between the loading rate of inorganic mercury and the target concentration of methylmercury in each compartment of the aquatic ecosystem. One of the projects focuses on a northern temperate lake in Wisconsin, while the other focuses on a subtropical marsh in the Everglades. WCA-3A has been chosen for this purpose. The required modeling to link mercury loads and concentrations in the Everglades ecosystem will be accomplished using a preliminary version of Everglades Mercury Cycling Model-2 under development by TetraTech, Inc. This effort is being jointly funded by USEPA, DEP, and the District.

## SFMSP BUDGET FOR FY00

The combined SFMSP budget for monitoring, research, modeling, assessment, and field validation studies, excluding permit compliance monitoring, is about \$6.25M for FY00. The District and DEP will contribute roughly \$0.85M and \$0.75M, respectively, while USEPA will contribute about \$3M, and USGS \$1.25M. The District has received a Clean Water Act Section 319 Grant from USEPA Region 4 via DEP for about \$150K to offset about 50 percent of the cost of mercury screening studies of the Advanced Treatment Technology projects now undergoing testing in the former ENR Project and its test cells. Other grant funding is also being sought by the District to further reduce the cost of mercury research, modeling, and assessment to the taxpayers of South Florida. In addition, as analytical capacity becomes available, DEP has agreed to perform ultra-trace mercury analysis of water, sediment, plants, and fish at no additional cost to the District to support mercury follow-up studies in the STAs and Florida Bay that are presently budgeted for commercial laboratory support.

# KEY FINDINGS AND RECOMMENDATIONS

These are the key management-relevant findings from the cumulative monitoring, research, modeling, and assessment studies conducted from 1989 to 1999.

## SOURCES

- Today's Everglades soil mercury levels are about three to six times those of the late 1800s.
- Sediment mercury patterns do not point to obvious local runoff or air source influence.

- Local incinerator reactive gaseous mercury (RGM) emissions are higher than expected.
- Landfills are potential big emitters of gaseous mercury species.
- EAA runoff contributes less than 5 percent of new mercury to the Everglades.
- Estimates of local air emissions source contributions to the annual atmospheric deposition load of total mercury to the Everglades still range from greater than 90 percent to less than 30 percent.
- Increases in the concentrations of RGM in the air can be detected at the eastern edge of WCA-3A when the wind blows out of the east for extended periods, suggesting a measurable influence of Ft. Lauderdale RGM sources.

## EXPOSURE AND EFFECTS

- Florida panthers feeding on southern Everglades raccoons were probably at significant mercury risks in late 1980s, but it has been claimed that there has been a decline in mercury levels in panthers over the last decade, although the data supporting that claim were not available as of this writing.
- Sunfish, shiners, shrimp, crayfish are a big portion of wading bird and bass diet, but not mosquitofish.
- Only subtle toxic effects were observed in great egret chicks dosed with methylmercury at levels that correspond to the concentrations in fish from the “hot spot” in WCA-3A.
- Field observations cannot detect a reduction in the reproductive success of the great egret colonies with the highest average mercury levels.
- Based on the District’s ecological risk assessment, WCA-2A-U3 (total phosphorus approx. 7 ppb) wading bird risks are unlikely to be unacceptable, but WCA-3A-15 (annual average total phosphorus approx. 5 ppb) wading bird risks may be. However, the water quantity and quality at WCA-3A are unlikely to change substantially in response to the ECP, so risk reduction will have to be brought about through local reduction of mercury air emission sources.

## BIOGEOCHEMISTRY PROCESSES

- Methylmercury is produced by sulfate-reducing bacteria in surface soils or some algal mats under low DO conditions.
- Methylmercury is decomposed via oxidative demethylation by methane-producing or carbon dioxide-producing bacteria depending on conditions.
- Sulfate, not phosphate, stimulates methylation, but sulfate is probably in excess of other limiting nutrients or short-chain carbon molecules required for sulfate-reducing bacteria metabolism.
- High sulfide in peat soil pore water is inversely correlated with the rate of methylmercury production, but the mechanism by which sulfide exerts this effect is not yet known.
- High phosphate stimulates high plant densities, production rates and decomposition rates, but dense rooted plant canopies can shade algae, breaking the link between the limiting nutrient and plant production.
- The increased dissolved oxygen associated with decrease of water column total phosphorus might be expected to move the zone of maximum methylation in peat soil deeper into the peat soil, reducing the methylmercury flux into the water column.
- Both inorganic mercury and methylmercury have high affinities for organic matter, whether in the form of dissolved or colloidal organic byproducts of plant decomposition (humic and fulvic acids), living or dead algae, fungi, or bacteria cell surfaces, plant detritus, unconsolidated colloidal floc, or consolidated peat soil.
- If allowed to reach steady state, inorganic mercury and methylmercury are distributed

amongst these aquatic ecosystem "compartments" according to their relative affinities for each compartment and the relative surface areas presented to the water by each compartment.

- However, the pulsed loading of inorganic mercury to the Everglades from rainfall and the pulsed nighttime production of methylmercury in response to those pulsed inorganic mercury loadings probably precludes the attainment of near steady state conditions, except perhaps in the dry season.
- High phosphate stimulates high plant densities, production rates and decomposition rates, which results in an average increase in settling/removal of both inorganic mercury and methylmercury from the water column and an average decrease in the concentration of inorganic mercury in the more rapidly accreting peat soil.
- High phosphate stimulates high plant densities, production rates, and decomposition rates, which results in a decrease in the average methylmercury concentrations in plant biomass and detritus and at each successive step in the food chain, a phenomenon sometimes referred to as biodilution.
- There is no known phosphorus-related process that accounts for the roughly three-fold greater concentrations of methylmercury in fish at WCA-3A-15 (annual average total phosphorus approx. 5 ppb) relative to WCA-2A (annual average total phosphorus approx. 7 ppb).
- The EAA is the primary contributor of excess sulfur to the northern Everglades, while local air emissions of oxides of sulfur (SOX) are probably the primary contributor of excess sulfur to the southern Everglades.
- The rate of methylmercury production in the Everglades is generally higher than other aquatic systems studied to date, but the ENR Project has the lowest methylmercury production rates measured anywhere in the Everglades.
- The rate of methylmercury production peaks in the middle of WCA-3A, while the rate of demethylation decreases steadily from north to south.
- The absolute and relative concentrations of sulfate and sulfide ion in Everglades peat pore water appear to be correlated with methylmercury production and bioaccumulation.

## ENR PROJECT PERFORMANCE

- The ENR Project, a prototype STA, had outflow water that never exceeded the Class III Water Quality Standard and was always less than inflow on an annual average basis.
- ENR Project interior and outflow fish were always less than reference site fish and have some of the lowest average mercury concentrations reported anywhere in the Everglades.
- Sediment total mercury did not reach hazardous levels and is declining overall, but there appears to be a reproducible two-year oscillation in the concentration of total mercury in the top 10 cm of the peat soil that has yet to be adequately explained.
- Over four full years of operation, the ENR Project removed 50 to 75 percent of total mercury from the inflow and rainfall and 50 to 75 percent of methylmercury from the inflow on an annual average basis.
- Rooted cattail emission of elementary mercury is substantial, perhaps the dominant loss pathway from the ENR Project, but the mechanism by which cattail transport elemental mercury from peat soil to air or the depth from which the mercury is being drawn are not yet known.

## PERFORMANCE OF NEW STAS

- At STA 6 following startup, total mercury and methylmercury in outflow or interior water and total mercury in interior and outflow fish sometimes exceed their corresponding concentrations in the inflow.

- At STA 1W, pre-startup Cell 5 interior water concentrations of total mercury and methylmercury exceed their corresponding concentrations upstream at S-5A, which has precluded startup as of this writing.
- STA 5 start-up occurred outside the 1998-1999 reporting period.

## ADVANCED TREATMENT TECHNOLOGIES

- The Submerged Aquatic Vegetation (SAV)-Limerock pilot system did not appear to discharge or concentrate methylmercury from the inorganic mercury present in wet and dry atmospheric deposition and inflow to any significant degree under the conditions encountered during the scoping study.
- Although the porta-PSTA pilot system screening study was not completed by the close of the reporting period, the early results of the porta-PSTA study indicate that it generally exhibited the same characteristics as the SAV-Limerock system.
- The Chemical Addition pilot system study was not begun until after the close of the reporting period. The results of the mercury screening study will be included in next year's Everglades Annual Report.

## ANSWERS TO KEY MERCURY MANAGEMENT QUESTIONS:

1. The Everglades mercury problem remains significant, but there is some evidence of a downward trend in mercury concentrations in fish and birds over the last decade at some Everglades locations.
2. Despite a reported 65 percent reduction in mercury air pollution from local sources over the last decade, there is still much uncertainty regarding the sources of the mercury depositing on the Everglades from air. Air pollution source, movement and chemistry studies should substantially reduce this uncertainty over the next two years.
3. The reduction in Everglades mercury risks is best achieved through reduction in mercury air pollution sources. The routing, timing, quantity and quality of water flowing into the Everglades will be optimized for the protection of Everglades structure and function, including endangered species habitat, so it is unlikely that there will be much flexibility for manipulating water quantity and quality to minimize methylmercury production and bioaccumulation, even if some options are potentially effective.
4. The District's updated ecological risk assessment continues to support last year's conclusion that it is highly unlikely that the operation of the STAs will cause or contribute to an environmentally significant increase in use impairment or mercury risks to fish-eating wildlife.
5. New monitoring, research and modeling tools have been developed to conduct the studies needed to understand and solve the Everglades mercury problem.
6. DEP endorsement of the Everglades Mercury Action Strategy (E-MAS) is being sought to ensure that the mercury restoration goal is achieved according to the Act's deadlines.

## STRATEGY FOR FILLING KEY SCIENCE DATA GAPS FOR SFMSP PHASE 2

The following are the key elements of the proposed strategy for filling the remaining information and tools gaps that preclude the development and implementation of a viable solution to the Everglades mercury problem at this time:

- Quantify wading bird diet-egg relationship to support a new methylmercury-based numerical Class III Water Quality Standard for total mercury.

- Quantify global vs local and new vs old mercury sources.
- Revise EMCM-1 to include food web uptake and P and S cycles and interactions with Hg cycle.
- Use new water quality standard and EMCM-2 to develop Everglades TMDL/WLA for Hg and S control.

The TMDL/WLA based on the revised WQS will then form the basis for water quality-based air emissions limits to protect the Everglades based on this scientific process. These limits will then be incorporated into the appropriate Clean Air Act permits. Consistent with this strategy, the following are key recommendations for SFMSP Phase 2 studies that are intended to reduce the uncertainty in the information obtained to date to levels that will support final restoration decision-making:

### New Water Quality Standard

- Measure dose-response probability distribution function (pdf) for several sensitive toxicological endpoints in the wading bird embryo, including teratogenesis and neurological development defects, retarded development, and low hatching weight and calculate wading bird egg no observable adverse effect level (NOAEL) for the most sensitive endpoint.
- Measure diet-egg ratios in laboratory using ration dosed with radiolabelled methylmercury and calculate diet-egg ratio pdf.
- Observe diet species-size foraging preferences and calculate size preference pdf.
- Quantify species size-concentration relationships and calculate pdf.
- Calculate combined pdf of dietary uptake of methylmercury from size-biased feeding preferences pdf and methylmercury size-concentration pdf.
- Calculate egg NOAEL-equivalent concentration pdf in diet from combined diet-egg ratio pdf and dose-response pdf.
- Clarify aquatic food web relationships and trophic assignments by adding crayfish and grass shrimp to the food web studies and by expanding isotope fractionation studies.
- Calculate biomagnifcation factors pdfs from food web studies.
- Calculate egg NOAEL-equivalent concentrations at each step in the food chain using biomagnifcation factor pdfs.
- Calculate egg NOAEL-equivalent methylmercury concentration in water pdf from combined dietary model pdf and food web model pdf.
- Select an appropriate level of protection for the most exposed, most sensitive piscivorous bird population.
- Read off the methylmercury water concentration from the combined pdf graph equivalent to the adopted level of protection.
- Adopt an appropriate margin of safety to compensate for any lack of knowledge about key relationships.
- Generate a pdf of the fraction of total mercury that is methylmercury for the Everglades.
- Convert the egg NOAEL-equivalent concentration of methylmercury in water to an equivalent concentration of total mercury in water using the preceding pdf.
- Promulgate a site-specific alternative criterion (SSAC) for the Everglades based on the above derivation process and result.

The District has requested commitments for matching federal and state funds to share the cost of the required toxicity and pharmacokinetics studies, existing plans have been determined not to be specific enough for purposes of preparing cost estimates. To remedy this deficiency, the District and DEP are co-sponsoring a workshop on methylmercury bioaccumulation, exposure, and toxicity to wading birds to address two issues. The first is the general issue of whether the methylmercury concentrations in the Everglades represent an unacceptable risk to some species at some locations.

The second issue relates to the most scientifically defensible, cost-effective way to obtain the understanding required for deriving a methylmercury criterion to protect Everglades wading birds, including the endangered wood stork. The recommendations of the wading bird workshop will guide the development, implementation, and interpretation of the results of the required toxicity and pharmacokinetics studies. The District will continue to seek co-funding and in-kind support from USGS, USEPA, U.S. Army Corps of Engineers, DEP, and FFWCC to conduct this critical work. In addition, outside grant funding is being sought to offset some of the costs of some of the required mercury research.

### TMDL Development

- Develop a EAA mass budget for mercury and each of the key influential factors
- Develop Everglades mass budgets for mercury and each of the key influential factors.
- Measure, then model water flows, stage-duration, and quality.
- Measure or calculate plant coverages and densities by species via remote sensing.
- Identify, qualify, and quantify the key processes governing the mercury cycle and the key physical, chemical, and biological factors influencing those key processes.
- Observe, measure, and model food web structure and species size-methylmercury concentration relationships.
- Translate qualitative and quantitative understanding of key processes and influential factors governing methylmercury production and bioaccumulation into equivalent mathematical functions.
- Revise EMCM-1 computer code to add key processes and factors governing the Everglades mercury cycle omitted from first version.
- Use four yrs. of ENR data to calibrate and test the upgraded model EMCM-2.
- Calculate mercury and influential factors load and concentration reductions at the point of discharge from each of the STAs to the District's canal system.
- Calculate the total mercury and methylmercury concentrations water, sediment, and fish in the impacted area downstream of the S-10 structures in WCA-2A, at the unimpacted site, WCA-2A-U3, and at the Everglades "hot spot", WCA-3A-15 with and without the effect of the STAs.

Each of the above elements is to be carried under Cooperative Agreement C-9694 with DEP to develop, calibrate, and apply the Everglades Mercury Cycling Model-2 from EMCM-1. The combined three-year funding commitment to this project is $300,000.

### Quantification of Non-abatable Soil Load

- Measure inorganic mercury soil species vertical concentration profiles.
- Measure soil depth of methylmercury production as a function of key influential factors.
- Develop functional definition and measures of, vertical concentration profiles of, and rates of release from refractory and labile inorganic mercury pools.
- Measure rates of net soil deposition and pore water DOC production.
- Measure or calculate diffusive, dispersive and advective fluxes of inorganic mercury and methylmercury across soil/water interface per physical, chemical, and biological conditions.

The qualitative and quantitative understanding required to achieve the above objectives is being obtained by USGS, although funding cuts in FY 2000 will severely limit the spatial coverage of the studies to be conducted in the Everglades. Some of this funding shortfall can be made up by an in-kind contribution of sample collection and shipment services by the District.

### Quantification of Nonabatable Global Background Air Load

- Obtain vertical profile of inorganic mercury species in air over South Florida up to top of free troposphere.
- Quantify of tall thunderhead scavenging efficiency of reactive gaseous mercury (RGM) from free troposphere.
- Calculate dry deposition velocities of RGM over open water and vegetation.
- Calculate natural background and anthropogenic global contributions to wet and dry deposition fluxes of Hg(II) via source, plume, and deposition studies and mass budget studies.
- Determine fraction of wet and dry Hg (II) deposition routed to refractory soil pools prior to methylation or reduction per physical, chemical, and biological conditions.

The studies required to achieve the above air source, transport, fate, and deposition objectives are being co-funded by DEP and USEPA. The required biogeochemical routing and kinetics studies are being conducted by USGS, although funding cuts in FY 2000 will severely limit the spatial coverage of the studies to be conducted in the Everglades. Some of this funding shortfall can be made up by an in-kind contribution of sample collection and shipment services by the District.

### Linkage Between Local Air Sources, Abatable Wet and Dry Deposition, and Receiving Water Quality

- Quantify local incinerator RGM and elemental mercury emissions rates as a function of feedstock composition, burn conditions, and throughput.
- Quantify RGM and elemental mercury transport in air emissions plumes via monitoring and modeling.
- Calculate potential wet and dry deposition load reduction under various local source reduction scenarios.
- Use EMCM-2 to evaluate reduction in methylmercury concentrations in water, sediment, and aquatic and terrestrial biota in response to wet and dry deposition load reduction under various local source reduction scenarios.

The studies required to achieve the above air source, transport, fate, and deposition objectives are being co-funded by DEP and USEPA. In some cases, the District is supplying in-kind support by providing access, building research platforms and providing portable electrical generators at remote sites.

## SYSTEM MONITORING

Monitoring of water and fish at key District structures and fish and birds at key interior marsh sites should continue to evaluate the responsiveness of total mercury supplies and methylmercury production and bioaccumulation to normal seasonal cycles and extreme events, especially following extended dry periods with or without associated fires. The addition of the otter and the reinstatement of the raccoon and Florida panther to this mercury monitoring program will ensure that the accurate tracking of mercury levels in a representative, highly exposed species from each step in the Everglades food chain. This will establish a baseline against which to evaluate the long-term positive and negative effects of local air pollution source controls and the ECP on the downstream mercury problem. This will also make possible an analysis of status and trends in bioaccumulation and exposures from which corresponding risks of toxic effects can be calculated for fish-eating animals and their predators.

## RECOMMENDATIONS

For the purpose of developing an accurate mercury cycling model of the Everglades, the process studies being conducted by the USGS should continue, but the emphasis should shift from primarily field surveys to controlled laboratory and field studies, including the effect of temperature on the key process rates. For the purpose of revising the total mercury standard, additional laboratory uptake, distribution and elimination (pharmacokinetics) studies should be conducted on the otter, the great egret as a substitute for the wood stork and the Texas cougar as a substitute for the Florida panther to supplement the applicable scientific literature. Continuing the exposure and effects studies of highly exposed wading birds in WCA-3A and Florida panthers in the Shark River Slough areas is necessary but not sufficient for this purpose. Analysis of fish, bird eggs, and alligator eggs for other persistent and bioaccumulative toxic substances in addition to total mercury will reduce the likelihood of confusing methylmercury toxic effects for those of other toxic substances present in the environment when interpreting field observation data.

## CLOSING REMARKS

This chapter has summarized management-relevant results from key monitoring, research, modeling and assessment studies completed as of April 30, 1999, and discussed the objectives of planned studies to fill data gaps identified in this exercise. The above research elements are intended to support a scientifically defensible regulatory process leading to the restoration of the use of the Everglades as a sport fishery and attainment and maintenance of the revised total mercury water quality standard. The Everglades Mercury Action Strategy (E-MAS) developed by the District is intended to guide that process. Mercury monitoring, research, modeling and assessment studies will continue to support adaptive management of the Everglades mercury problem. In the interim, this chapter has provided ongoing assurance that it is highly unlikely that the ECP will cause or contribute to an environmentally significant increase in mercury risks to fish-eating wildlife in the already impacted areas of the Everglades or the unimpacted areas downstream.

# LITERATURE CITED

Aiken, G. and M. Reddy, 1997. Dissolved organic carbon in the Everglades, Florida. US Geological Survey, 3215 Marine Street, Boulder, CO, at the Second Annual Everglades Mercury Workshop, Edgewater Hotel, Madison, Wisconsin. May.

Ambrose, Jr., R.B. and R. Araujo, 1998. Applications of the Phase I Everglades Mercury Cycling Model. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA, at the Third Annual Everglades Mercury Workshop, Sheraton West Palm Beach Hotel, West Palm Beach, FL. May.

Bates, A.L., W.H. Orem, and J.W. Harvey, 1998. Tracing sources of sulfate in the northern Everglades using sulfur isotopic compositions, EOS, Transactions, American Geophysical Union, Spring Meeting, Program and Abstracts, May 26-29, Boston, MA.

Beijer, K., and A. Jernelov, 1979. Methylation of mercury in aquatic environments. In J. O. Nriagu (ed) The Biogeochemistry of mercury in the Environment. Elsevier/North Holland Biomedical Press, New York.

Benoit, J.M., W.F. Fitzgerald and A.W.H. Damman, 1994. Historical atmospheric mercury deposition in the mid-continental U. S. as recorded in an ombrotrophic peat bog. Pages 187-202 in C.J. Watras and J.W. Huckabee, editors. Mercury Pollution Integration and Synthesis, Lewis Publishers, Boca Raton, FL.

Benoit, J.M., C.C. Gilmour, R.P. Mason, and A. Heyes, 1999. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Env. Sci. Technol. 33(6): 951-957.

Benoit, J.M., R.P. Mason, and C.C. Gilmour, 1999. Estimation of mercury-sulfide speciation in sediment pore waters using octanol-water partitioning and its implications for availability to methylating bacteria. J. Env. Toxicol. Chem. 8 (10): 2138-2141.

Bouton, S.N, P.C. Frederick, M.G. Spalding and H. McGill, 1999. Effects of chroic, low concentration of dietary methylmercury on the behavior of juvenile great egrets. J. Env. Toxicol. Chem. 18(9): 1934-1939.

Brezonik, P.L., 1984. Trophic state indices: Rationale for multivariate approaches. Pages 441–445. In Lake and Reservoir Management: Proc. 3rd Ann. Conf. N. Amer. Lake M. Soc. Knoxville, Tenn. EPA 440/5/84-001. USEPA. Washington, DC.

CDC, 1994. Mercury exposure among the Miccosukee Indian Tribe: South Florida, 1993. USDHHS, USPHS, Division of Environmental Hazards and Health Effects, National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, GA. 12 pp., typescript.

Carlson, R.E., 1980. Using trophic state indices to examine the dynamics of eutrophication. Pages 218-21 in Restoration of Lakes and Inland Waters. Proc. Int. Symp. Inland Waters and Lake Restoration. Portland, Maine. EPA 440/5-81-010. USEPA, Washington, DC.

Clarkson, T.W., 1994. The toxicology of mercury and its compounds. 1994. Pages 631-639 in C.J. Watras and J.W. Huckabee, editors. Mercury Pollution: Integration and Synthesis. Lewis Publishers, Boca Raton, FL.

Cleckner, L. B., C. C. Gilmour, J. P. Hurley, and D. P. Krabbenhoft, 1999. Mercury methylation in periphyton of the Florida Everglades. Limno. Oceanogr. 44(7): 1815-1825.

D'Itri, F.M., C.S. Annett and A.W. Fas, 1971. Comparison of mercury levels in an oligotrophic and eutrophic Lake. J. Mar. Technol. Soc. 5(6): 10-14.

Davis, S.M., 1989. Sawgrass and cattail production in relation to nutrient supply in the Everglades. in Freshwater Wetlands and Wildlife, R.R. Sharitz and J.W. Gibbons (Eds), USDOE, Oak Ridge.

Davis, S., 1991. Growth, decomposition, and nutrient retention of *Cladium jamaicense Crantz* and *Typha domingensis pers.* in the Florida Everglades. Aquatic Botany 40: 203-224.

Delfino, J.J., T.L. Crisman, J.F. Gottgens, B.R. Rood and C.D.A. Earle, 1993. Spatial and temporal distribution of mercury in Everglades and Okefenokee wetland sediments. Final Project Report (April 1, 199 -June 30, 1993) to South Florida Water Management District (contract no. C91-2237), USGS (contract no. 14-08-0001-G-2012) and Florida DER (contract no. WM415).

Delany, M.F., J.U. Bell, and S. Sundlof, 1988. Concentrations of contaminants in muscle of the American alligator in Florida. J. Wildlife Diseases 24 (1): 62-66.

Dvonch, J.T., J.R. Graney, G.J. Keeler, and R.K. Stevens, 1999. Use of elemental tracers to source apportion mercury in South Florida perceipitation. Env. Sci. and Technol. In press.

Ehrlich, P.R., A.H. Ehrlich, and J.P. Holdren. Ecoscience: Population, Resources, Environment. Freeman, NY., 1977. p. 574

Engebretson, R.R. and R. Von Wandruszka, 1998. Kinetic aspects of cation-enhanced aggregation in aqueous humic acids. Env. Sci. and Technol. 32(4): 488-493.

Evans, D.W. and D.W. Engel, 1998. Origin of elevated mercury concentrations from eastern Florida Bay: Progress Report. NOAA/Center for Coastal Fisheries Habitat Research, Beaufort Laboratory. Beaufort, North Carolina.

Exponent (formerly PTI), 1998. Ecological Risks to Wading Birds of the Everglades in Relation to Phosphorus Reductions in Water and Mercury Bioaccumulation in Fishes. Exponent, 15375 SE 30th Place, Suite 250, Bellevue, WA 98007. Prepared for the Sugar Cane Growers Cooperative of Florida, P.O. Box 666, Belle Glade, FL 33430. June.

Fink, L.E., D. Rumbold, and P. Rawlik, 1999. "Chapter 7: The Everglades Mercury Problem." The Everglades Interim Report to the Florida Legislature. South Florida Water

Management District, West Palm Beach, FL. January.

Fink, L.E. and P.S. Rawlik, 1998. Screening-level ecological risk assessment for mercury in the Everglades. Water Resources Evaluation Department, South Florida Water Management District, West Palm Beach, FL, at the Third Annual Everglades Mercury Workshop, Sheraton West Palm Beach Hotel, West Palm Beach, FL. May.

Fitzgerald, W.F., 1989. Atmospheric and oceanic cycling of mercury. Pages 151-186 in J.P. Riley and R. Chester, editors. Chemical Oceanography 10. Academic Press, NY.

Fleming, L.E., S. Watkins, R. Kaderman, B. Levin, D.R. Ayyar, M. Bizio, D. Stephens, and J.A. Bean, 1995. Mercury exposure to humans through food consumption from the Everglades of Florida. Water, Air and Soil Pollution 80: 41-48.

Frederick, P.C., M.G. Spalding, M.S. Sepulveda, G.E. Williams, Jr., S.M. Lorazel and D.A. Samuelson, 1997. Effects of elevated mercury on reproductive success of long-legged wading birds in the Everglades. Final Report of the University of Florida to the Florida Department of Environmental Protection, Tallahassee, FL. August.

Frederick, P.C., M.G. Spalding, M.S. Sepulveda, G.E. Williams, L. Nico and R. Robins, 1999. Exposure of great egret (Ardea albus) nestlings to mercury through diet in the Everglades ecosystem. J. Env. Toxicol. Chem. 18(9): 1940-1947.

Gilmour, C.C. and E.A. Henry, 1991. Mercury methylation in aquatic systems affected by acid deposition. Environ. Pollut. 71: 131.

Gilmour, C.C., E.A. Henry and R. Mitchell, 1992. Sulfate stimulation of mercury methylation in sediments. Environ. Sci. Technol. 26: 2281-2287.

Gilmour, C.C., G.S. Ridel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill and M.C. Stordal, 1998a. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry. 40: 327-345.

Gilmour, C.C., A. Heyes, J. Benoit, G. Reidel, J.T. Bell and G.Gill, 1998b. Distribution and biogeochemical control of mercury methylation in the Florida Everglades. Annual Report for 1998. Academy of Natural Sciences, Estuarine Research Center, St. Leonard, MD. Contract C-7690 with the South Florida Water Management District. June.

Grieb, T.M., C.T. Driscoll, S.P. Gloss, C.L. Schofield, G.L. Bowie, D.B. Porcella, 1990. Factors affecting mercury accumulation in fish in the upper Michigan peninsula. Environ. Toxicol. Chem. 9: 919:930

Grimshaw, H. J., R.G. Wetzel, M. Brandenburg, K. Segerblom, L.J. Wenkert, G.A. Marsh, W. Charnetzky, J.E. Haky, and C. Carraher, 1997. Shading of periphyton communities by wetland emergent macrophytes: Decoupling of algal photosynthesis from microbial nutrient retention. Arch. Hydrobiol. 139 (1): 17-27.

Haag, K.H and B.F. McPherson., 1997. Organochlorine pesticides and PCBs I southern Florida fishes: then and now. Fact Sheet. U.S. Geologial Survey, St. Petersburg, FL.

Hakanson, L., 1980. The quantitative impact of pH, bioproduction and Hg-contamination on the Hg- content of fish (pike). Environ. Pollut. (Series B) 1: 285-304.

Harvey, J.W., S.L. Krupa, C.J. Gefvert, J. Choi, R.H. Mooney and J.B. Giddings., 1999. Interaction between ground water and surface water in the northern Everglades and the relation to water budgets and mercury cycling. Final Report for Cooperative Agreement C-6661. August.

Heaton-Jones, T.G., B.L. Homer, D.L. Heaton-Jones, and S.F., Sundlof, 1997. Mercury distribution in American alligators (alligator mississippiensis) in Florida. J. Zoo and Wildlife Medicine 28: 62-70.

Heinz, G.H., 1979. Methyl mercury: Reproductive and behavioral effects on three generations of mallard ducks. J. Wildl. Manage. 43: 394-401.

Heinz, G. H., H. F. Percival, M. L. Jennings, 1991. Contaminants in American alligator eggs from Lake Apopka, Lake Griffin, and Lake

Okeechobee, Florida. Env. Monitoring and Assessment 16: 277-285.

Hord, L.J., M. Jennings, and A., Brunell, 1990. Mercury contamination of Florida alligators. pp. 229- 240. In Crocodiles. Proceedings of the 10th Working Meeting of the Crocodile Specialist Group, Volume 1. IUCN-The World Conservation Union, Gland, Switzerland.

Humphrey, S.R. (ed), 1992. Rare and Endangered Biota of Florida: Volume I. Mammals. University Press of Florida, Gainesville.

Hurley, J.P., D.P. Krabbenhoft, L.B Cleckner, M.L. Olson, G. Aiken and P.J. Rawlik, Jr., 1998. System controls on aqueous mercury distribution in the northern Everglades, Biogeochemistry 40: 293-311.

Hurley, J.P., L.B. Cleckner, and P. Gorski, 1999. Everglades Nutrient Removal Project Mosquitofish Bioaccumulation Study. Draft Report. Prepared for the South Florida water Management District, West Palm Beach, FL. Contract (PC C-8691-0300). University of Wisconsin Water Chemistry Program, Madison, WI. May.

Jensen, S. and A. Jernelov, 1969. Biological methylation of mercury in aquatic ecosystems. Nature. 223: 753-754.

Jurczyk, N.U., 1993. An ecological risk assessment of the impact of mercury contamination in the Florida Everglades. University of Florida, Gainesville, FL.

Kannan, K., R.G. Smith Jr., R.F. Lee, H.L.Windom, P.T. Heitmuller, J.M. Macauley, and J.K. Summers, 1998. Distribution of total mercury and methyl mercury in water, sediment, and fish from south Florida Estuaries. Arch. Environ. Contam. Toxicol., 34: 109-118.

Kilham, L., 1984. American crows feeding on and storing river otter dung. Fl. Field Naturalist 12 (4): 10

King, S., 1999. Ph.D. Dissertation. University of Wisconsin, Madison, Wisconsin.

Krabbenhoft, D.P., J.P. Hurley, M.L. Olson and L.B. Cleckner, 1998. Diel variability of mercury phase and species distributions in the Florida Everglades. Biogeochemistry 40: 311-325.

Lange, T.R., D.A. Richard and H.E. Royals, 1998. Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. FINAL Annual Report. Florida Game and Fresh Water Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL. April.

Lange, T.R., D.A. Richard and H.E. Royals, 1999. Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. Annual Report. Florida Game and Fresh Water Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL. April.

Lindberg. S.E., A. Vette, C. Miles and F. Schaedlich, 1998. Application of an automated mercury analyzer to field speciation measurements: Results for dissolved gaseous mercury in natural waters. Geochimica et Cosmochimica Acta. In Press.

Loftus, W.F., J.C. Trexler, R.D. Jones, 1998. Mercury Transfer Through and Everglades Aquatic Food Web. Report to Fl. Dept. of Environmental Protection, Tallahassee.

Maehr, D.S., R.C. Belden, E.D. Land, and L. Wilkins., 1990. Food habits of panthers in southwest Florida. J. Wildlife Management. 54(3): 420-423.

Marsik, F.J., K.I Al-Wali, G.J. Keeler, R Bullock and R. Draxler. 1999. Modeling of the Annual Impact of Local and Regional Emissions of Mercury on South Florida. Abstract. Annual Workshop of the South Florida Mercury Science Program. Sheraton Buckhead Hotel, Atlanta, GA. June.

Marvin-DiPasquale, M.C. and R.S. Oremland, 1998. Bacterial methylmercury degradation in Florida Everglades peat sediment. Environ. Sci. Technol. 32(17): 2556-2563.

Mason, R. and A. Lawrence, 1999. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore

Harbor, Maryland, USA. Environmental Toxicology and Chemistry 18(11): 2438-2447.

Maurice, P.A. and K. Namjesnik-Dejanovic, 1999. Aggregate structures of sorbed humic substances observed in aqueous solution. Env. Sci. and Technol. 33(9): 1538-1541.

Mauro, J.B.N., and J.R.D. Guimaraes, 1999. Hg methylation potential in aquatic macrophytes of the Everglades Nutrient Removal Area. Report to the South Florida Water Management District, W. Palm Beach

McCormick, P.V., R.B.E. Shuford III, J.G. Backus, and W.C. Kennedy, 1998. Spatial and seasonal patterns of periphyton biomass and productivity in the northern Everglades, Florida, U.S.A. Hydrobiologia 362: 185-208.

Miao, S. L. and F. H. Sklar, 1998. Biomass and nutrient allocation of sawgrass and cattail along a nutrient gradient in the Florida Everglades. Wetlands Ecology and Management 5: 245-263.

Miles, C.J. and L.E. Fink, 1998. Monitoring and mass budget for mercury in the Everglades Nutrient Removal Project. Archives of Environ. Contam. and Toxicol. 35(4): 549-557.

Norstrom, R.J., A.E. McKinnon and A.S.W. DeFreitas, 1976. A bioenergetics-based model for pollutant accumulation by fish. Simulation of PCB and methylmercury residue levels in Ottawa River yellow perch (*Perca flavescens*). J. Fish Res. Board Can. 33: 248-267.

O'Connor, D.J and S.W. Nielsen, 1981. Environmental survey of methylmercury levels in wild mink (Mustela vison) and otter (Lutra canadensis) from the northeatsern United Sattes and experimental pathology of methylmercurialism in the otter. Proc. Worldwide Furbearer Conference, Frostburg, MD, USA. Agust 3-11: 1728-1745.

Ogden, J.C., J. Kushlan, and J.T. Tilmant, 1978. The food and nesting success of wood storks in the Everglades National Park, 1974. Natural Resources Report 16. USDOI, National Park Service, Washington, D.C.

Ogden, J.C., W. B. Robertson, Jr., G.E. Davis, and T.W. Schmidt, 1974. Pesticides, Polychlorinated Biphenols and Heavy Metals in Upper Food Chain Levels, Everglades National Park and Vicinity. Division of Natural Science and Resource Management Studies, Everglades National Park.

Olson, B.H. and R.C. Cooper, 1976. Comparison of aerobic and anaerobic methylation of mercuric chloride by San Francisoco Bay sediments. 10: 113-116.

PTI., 1995a. Ecological Risks to Wading Birds of the Everglades in Relation to Phosphorus Reductions in Water and Mercury Bioaccumulation in Fishes. PTI Contract C663. Prepared for Hopping Green Sams and Smith, 123 South Carolina Street, Tallahassee, FL 32301 and Sugar Cane Growers Cooperative of Florida, P.O. Box 666, Belle Glade, FL 33430. January.

PTI, 1995b. Ecological Risks to Wading Birds of the Everglades in Relation to Phosphorus Reductions in Water and Mercury Bioaccumulation in Fishes. PTI Contract C663. Prepared for Hopping Green Sams and Smith, 123 South Carolina Street, Tallahassee, FL 32301 and Sugar Cane Growers Cooperative of Florida, P.O. Box 666, Belle Glade, FL 33430. June.

PTI, 1997. Ecological Risks to Wading Birds of the Everglades in relation to Phosphorus Reductions in Water and Mercury Bioaccumulation in Fishes. Handout to the Florida Environmental Regulation Commission, Tallahassee, FL. PTI Environmental Services, Waltham, MA. Prepared for Hopping Green Sams and Smith, 123 South Carolina Street, Tallahassee, FL 32301 and Sugar Cane Growers Cooperative of Florida, P.O. Box 666, Belle Glade, FL 33430. January 31, 1997.

Patrick, W.H., Jr., R.P. Gambrell, P Parkpian and F. Tran., 1994. Mercury in soils and plants in the Florida Everglades sugarcane area. Pages 609-620 in C. J. Watras and J. W. Huckabee, editors. Mercury Pollution: Integration and Synthesis. Lewis Publishers, Boca Raton, FL.

Peters, L.J., 1983. Mercury accumulation in the american alligator, *Alligator mississippiensis.* Masters Thesis. University of Florida, Gainesville, FL.

Post, G.W., 1983. Textbook of Fish Health. T.F.H. Publications, Neptune City, NJ.

Plette, A.C.C., M.M. Nederlof, E.J.M. Temminghoff and W.H. van Riemsdijk, 1999. Bioavailability of heavy metals in terrestrial and aquatic ecosystems: a quantitative approach. Env. Toxicol. Chem. 18(9):1882-1890.

Rader, R.B., 1994. Macroinvertebrates of the northern Everglades: Species composition and trophic structure. Florida Scientist 57 (1,2): 22-33.

Ravichandran, M., G.R. Aiken, M.M. Reddy and J.N. Ryan., 1998. Enhanced dissolution of cinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. Ennv. Sci. Technol. 32: 3205-3311.

Ravichandran, M., 1999. Interactions between mercury and dissolved organic matter in the Florida Everglades. Ph.D. Thesis. University of Colorado. Spring.

Rawlik, P., 1999. Intercomparison of Ultra-trace Mercury Analytical Capability. Tech. Pub. WRE-709. South Florida Water Management District, West Plam Beach, Florida.

Reddy, M.M., G. Aiken, P.F. Schuster, 1999. Hydroperiod-Driven Solute Transport at the Peat-Water Interface in the Florida Everglades: Hydrophobic Acid Diffusion from Peat. Unpublished Mansucript. U.S. Geological Survey, Boulder, CO. June.

Reddy, K.R., W.F. DeBusk, Y. Wang, R. DeLaune, M. Koch., 1991. Physico-Chemical Properties of Soils in the Water Conservation Area 2 of the Everglades. University of Florida, Gainesville.

Rodgers, D.W., 1994. You are what you eat and a little bit more: bioenergetics-based models of methylmercury accumulation in fish revisited. In C.J. Watras and J.W. Huckabee, Mercury Pollution Integration and Synthesis, Lewis Publishers, Boca Raton: 427-439.

Roelke, M.E. and Glass, C.M, 1992. Florida Panther Biomedical Investigation. Annual Performance Report on Statewide Wildlife Research: 1 July 1991-30 June 1992. Study E-1-II-E-6. Florida Game and Fresh Water Fish Commission, Tallahassee, FL.

Robertson, A.P. and J.O. Leckie, 1999. Acid/base copper binding, and Cu2+/H+ exchange properties of a soil humic acid, an experimental and modeling study. Env. Sci. and technol. 33(5): 786-795

Rudd, J.W.M., and M.A. Turner, 1983. The English-Wabigoon River System: V. Mercury and selenium bioaccumulation as a function of aquatic primary productivity. Can. J. Fish. Aquat. Sci. 40: 2251-2259.

Rumbold, D. and L.E. Fink, 1999. Confounding Evidence for the "Inverse Relationship" in Everglades Interim Report Appendices (as Appendix 7-4) SFWMD, West Palm Beach.

Rumbold, D., P. Rawlik, and L. Fink, 1999. "Ecological Risk Assessment of Mercury in the Florida Everglades: Risks to Wading Birds," Appendix 7-2 in The Everglades Interim Report to the Florida Legislature, South Florida Water Management District, West Palm Beach, FL. January.

Rutchey, K. and L. Vilchek, 1994. Development of an Everglades vegetation map using a SPOT image and the Global Positioning System. Photogrammetric Engineering and Remote Sensing 60: 767-775.

Ryder, R.A., 1950. Great blue heron killed by carp. Condor 52(1): 40-41.

SFWMD, 1999a. Everglades Nutrient Removal Project 1998 Monitoring Report. South Florida Water Management District, West Palm Beach, FL. March.

SFWMD, 199b. Final Report on the Effect of Best Management Practices on the Loading of Mercury Species to/from the Everglades Nutrient Removal Project: Monitoring Program (Project C-1). Submitted by the South Florida Water Management District, West Palm Beach, Florida, to the Florida Department of Environmental Protection, Tallahassee, Florida, to fulfill the requirements of a Section 319 Grant (SP335/C-6663/4) from U.S. Environmental Protection Agency Region 4, Atlanta, GA.

SSG, 1997. Ecologic and Precursor Success Criteria for South Florida Ecosystem Restoration. Science Sub-Group Report to the Working Group of the South Florida Ecosystem Restoration Task Force. May

Sample, B.E. and G.W. Suter II, 1999. Ecological risk assessment in a large river-reservoir: 4. Piscivorous Wildlife. Env. Tox. and Chem. 18 (4): 610-620.

Sanchez, C.A., 1990. Soil-testing and Fertilization Recommendations for Crop Production on Organic Soils in Florida. Bulletin 876. Agricultural Experimental Station, Institute for Food and Agricultural Sciences, University of Florida, Gainesville. June. P 30.

Sellers, P., C.A. Kelly, J.W.M. Rudd, A.R. MacHutchon, 1996. Photodegradation of methylmercury in lakes. Nature 380(25): 694-697.

Sepulveda, S.M., H. Robert, R.H. Poppenga, J.J. Arrecis, L.B. Quinn, 1998. Concentrations of mercury and selenium in tissues of double cretsed cormorants from southern Florida. Florida Wildlife. 21:35-42.

Smith, A.T., 1980. An Environmental Study of Everglades Mink (*Mustela vison*). South Florida Research Center, Everglades National Park.

Smith, A.T. and D.M. Cary, 1982. Distribution of Everglades Mink. Florida Scientist 45 (2): 106-112.

Stoneburner, D.L. and J.A. Kushlan, 1984. Heavy metal burdens in American crocodile eggs from Florida Bay, Florida, USA. J. Herpetology 18 (2): 192-193.

Strom, D. and G. Graves, 1995. Mercury Levels in Marine Fishes in South Florida. Florida Department of Environmental Protection, Pt. St. Lucie, FL. October.

Sundlof, S.F., M.G. Spalding, J.D. Wentworth, and C.K. Steible, 1994. Mercury in the liver of wading birds (Ciconiiformes) in southern Florida. Arch. Environ. Cont. Toxicol. 27: 299-305.

Sugar Cane Growers Cooperative, 1999. Letter from George Wedgworth, President, Sugar Cane Growers Cooperative, to Michael Collins, Chairman, Governing Board, South Florida Water Management District, and others. Belle Glade, FL. May 20.

Swift, D.R. and R.B. Nicholas, 1987. Periphyton and water quality relationships in the Everglades Water Conservation Areas, 1978-1982. Tech. Pub. 87-2. SFWMD, West Palm Beach, FL.

Tsiros, I.X., and R.B. Ambrose, 1999. An environmental simulation model for transport and fate of mercury in small rural catchments. Chemosphere. 39(3): 477-492.

USEPA, 1980. An Exposure and Risk Assessment for Mercury. Final Draft Report. Office of Water Regulations and Standards, U.S. Environmental Protection Agency, Washington, DC. August.

USEPA, 1993. Great Lakes Water Quality Criteria. U.S. Environmental Protection Agency Region 5, Chicago, IL.

USEPA, 1997. Mercury Study Report to Congress. Volume 1: Executive Summary. Office of Air Quality Planning and Standards and Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C., EPA-452/R-97-003. December.

USEPA, 1998. South Florida Ecosystem Assessment. Volume 1. Technical Report. Monitoring for adaptive management: Implications for ecosystem restoration. Region 4 and Office of Research and Development, Athens, GA. December. EPA-904-R-98-XXX.

Vaithiyanathan, P., C.J. Richardson, R, G. Kavanaugh, C.B. Craft and T. Barkay, 1996. Relationships of eutrophication to the distribution of mercury and the potential for methylmercury production in the peat soils of the Everglades. Environ. Sci. Technol. 30(8): 2591-2597.

Vaughan, P.P. and N.V. Blough, 1998. Photochemical formation of hydroxyl radical by constituents of natural waters. Env. Sci. and Technol. 32(19): 2947-2953.

WHO, 1976. Environmental Health Criteria 1: Mercury. World Health Organization. Geneva.

Ware, F.J., H. Royals and T. Lange, 1991. Mercury contamination in Florida largemouth bass. Florida Game and Fresh Water Fish Commission, Tallahassee, FL.

Ware, F., 1989. Unpublished report. Florida Game and Fresh Water Fish Commission to the Florida Department of Environmental Regulation, Tallahassee, FL. July.

Watras, C. 1993. Potential impact of the Everglades Nutrient Removal Project on the Everglades mercury problem. (EV 930034). Unpublished report prepared for the South Florida Management District. University of Wisconsin, Madison, WI. October.

Watras, C.J. et al., 1994. Sources and fates of mercury and methylmercury in Wisconsin lakes. in C.J. Watras and J.W. Huckabee [eds]. Mercury as a Global Pollutant: Toward integration and Synthesis. Lewis, Boca Raton, F: 153-177.

Winfrey, M.R. and Rudd, J.W.M., 1990. Environmental factors affecting the formation of methylmercury in low pH lakes. Environ. Toxicol. Chem. 9: 853.

Wobeser, G., N.O. Nielsen, B. Schiefer, 1976. Mercury and mink II. Experimental methyl mercury intoxication. Can. J. Comp Med 40:34-45.

Wolfe, M.F., S. Schwarzbach, and R.A. Sulaiman, 1998. Effects of mercury on wildlife: a comprehensive review. J. Env. Tox. Chem. 17(2): 146-160.

Wood, J.M. 1974. Biological cycles for toxic elements in the environment. Science 183: 1 049-1 052.

Xia, K, U.L. Skyllberg, W.F. Bleam, P.R. Bloom, E.A. Nater and P.A. Helmke, 1999. X-ray absorption spectroscopic evidence for the complexation of Hg(II) by reduced sulfur in soil humic substances. Env. Sci. and Technol. 33(5): 786-795.

Yanochko, G.M., C.H. Jagoe, and I. L. Brisbin, Jr., 1997. Tissue mercury concentrations in alligators (*Alligator mississippiensis*) from the Florida Everglades and the Savannah River Site, South Carolina. Arch. Environ. Toxicol. 32: 323-328.